GROUP IV METAL COMPLEXES OF NITROGEN CONTAINING LIGANDS

ABSTRACT

A THESIS
SUBMITTED TO THE ALIGARH MUSLIM UNIVERSITY, ALIGARH
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY

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ABSTRACT

Donor-acceptor type of complexes of some tetrahalides of group (IV) elements, viz., silicon (IV) chloride, germanium (IV) chloride, tin (IV) fluoride, tin (IV) chloride, tin (IV) bromide, tin (IV) iodide, titanium (IV) fluoride, titanium (IV) chloride, zirconium (IV) fluoride and zirconium (IV) chloride, with pyrazolones, piperazine bis-dithiocarbamate and benzoquinolines have been synthesized and characterized. The composition of the solid complexes has been established on the basis of elemental analysis. Infrared spectral studies (4000-200 cm^{-1}) have been made to elucidate the structure and stereochemistry of the complexes. Changes in the IR frequencies of different group upon coordination have been studied and the coordination sites proposed. The far infrared spectra of the complexes in the region 650-200 cm^{-1} have been recorded to assign the metal-halogen stretching vibrations and to establish, therefrom, their stereochemistry. The molar conductances of the soluble complexes have been measured and indicate that they are basically non-ionic in nature.

The complexes of pyrazolones, viz., antipyrine (ap) and 4-aminoantipyrine (aap), of the type $MX_4(ap)_2$ [for M = Sn; X = Br, I and for M = Ge, Zr; X = Cl] and $MX_4(aap)_n$ [for M = Sn; X = Cl, Br, I; n = 1 and for M = Ge, Ti, Zr; X = Cl; n = 2] have been synthesized to study the coordination behaviour of

pyrasolones and to establish the structure of the complexes. The IR spectra indicate coordination through carbonyl oxygen in all the complexes. In 1:1 complexes of 4-aminoantipyrine the amino group is also found to be coordination active. In 1:2 (MX_4:ligand) complexes the presence of only one ν (M-X) band in the far IR region is indicative of a trans-octahedral geometry. However, in $GeCl_4$ complex of 4-aminoantipyrine four ν(Ge-Cl) bands attributable to a cis-octahedral geometry are observed. The tin (IV) chloride and bromide complexes of 4-aminoantipyrine formed in a 1:1 ratio also have only one M-X stretching frequency band at 330 and 240 cm^{-1}, respectively. A polymeric trans-octahedral structure involving ligand bridging through the carbonyl oxygen and the amino nitrogen is proposed for these complexes.

The complexes of piperazine 1,4-dicarbodithioate (piperazine bis-dithiocarbamate, Pzdtc) of the type SnX_2(Pzdtc) [X = F, Cl, Br, I], MX_2H_2(Pzdtc)$_2$ [for M = Ge, Si; X = Cl; for M = Ti; X = F, Cl and for M = Zr; X = F] and Zr_2Cl_6(Pzdtc) have been synthesized to study whether it acts as an unidentate, bidentate or multidentate ligand and to establish the structures of such complexes. The IR studies revealed that piperazine bis-dithiocarbamate acts as a quadridentate ligand in tin (IV) fluoride, tin (IV) chloride, tin (IV) bromide, tin (IV) iodide

and zirconium (IV) chloride complexes and as a bidentate ligand in the remaining complexes leaving another CS_2^- group uncoordinated to which a proton is attached. A hexacoordinated polymeric structure involving ligand bridging through dithiocarbamate group is proposed for tin (IV) complexes. An octahedral trans-configuration is suggested for the $MX_2L_2(Pzdtc)_2$ type of complexes.

Benzo (f) quinoline (bfq) complexes of the general formula $MX_4(bfq)_n$ [for M = Sn (X = F, I), Si (X = Cl), Ti (X = F, Cl); n = 2 and for M = Sn (X = Cl, Br), Ge (X = Cl), Zr (X = F, Cl); n = 1] have been synthesized to study the nature of bonding of the metal to the ligand. In benzo (f) quinoline the coordination site is only the ring nitrogen atom. The ν(M-N) vibrations appear in the 295-335 cm^{-1} region. Appearance of only one ν(M-X) band in the $SnF_4(bfq)_2$, $SiCl_4(bfq)_2$, $TiF_4(bfq)_2$ and $TiCl_4(bfq)_2$ complexes at 550, 425, 560 and 428 cm^{-1}, respectively indicates a trans-octahedral environment of the metal ion in these complexes. In the $SnCl_4(bfq)$ and $GeCl_4(bfq)$ complexes both terminal and bridging ν(M-X) vibration bands have been observed and a hexacoordinated octahedral structure involving halogen bridging has been proposed for these complexes.

The complexes of benzo (c) quinoline (phenanthridine, beq) of the type $MX_4(beq)_n$ [for M = Sn (X = F, Br, I); Zr, Si (X = Cl), Ti (X = F, Cl); n = 2 and for M = Sn, Ge (x = Cl), Zr (X = F);

n = 1] have been synthesised and characterized. The ring nitrogen atom is the only coordination site in this ligand and ν(M-N) vibrations appear in the 308-345 cm^{-1} region in its complexes. In the $SnF_4(beq)_2$, $SiCl_4(beq)_2$, $TiF_4(beq)_2$ $TiCl_4(beq)_2$ and $ZrCl_4(beq)_2$ complexes the appearance of only one ν(M-X) vibration band at 540, 445, 500, 375 and 348 cm^{-1}, respectively, indicates a trans-octahedral geometry for these complexes. In the IR spectra of $SnCl_4(beq)$, $GeCl_4(beq)$ and $ZrF_4(beq)$ both terminal and bridging ν(M-X) vibration bands are detectable and an octahedral structure involving halogen bridged bonds has been suggested for these complexes.

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Certified that the work embodied in this thesis entitled "Group IV Metal Complexes of Nitrogen Containing Ligands" is the result of original researches carried out under my supervision by (Mrs.) Nikhat Sultana Neelam and is suitable for submission for the award of the Ph.D degree of Aligarh Muslim University, Aligarh.

(S.A.A. Zaidi)
Professor of Chemistry

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C O N T E N T S

PUBLICATIONS

1. Complexes of group (IV) metal halides with piperazine 1,4-dicarbodithioate,

   S.A.A. Zaidi, T.A. Khan and N.S. Neelam, Indian Journal of Chemistry (In press).

2. Complexes of group (IV) halides with antipyrine and 4-aminoantipyrine,

   S.A.A. Zaidi, T.A. Khan and N.S. Neelam, Proc. Annual Convension of Chemists, ING-48, pp.27 (1977).

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CHAPTER - I

I N T R O D U C T I O N

INTRODUCTION

During recent years the complexes of group (IV) metal halides have been studied in detail due to their importance in our day to day life. In our environment no family of elements is more important than the members of group (IV) elements. Thus, while on the one hand the carbon-carbon bond completely dominates the animal and vegetable world, compounds with the silicon-oxygen bond form a major part of the mineral world on the other. Industrially tin and lead compounds are not as important as the metals themselves. Germanium, the rarest element of the family which was a laboratory curiosity for the last fifty years, has recently been in great demand because of its use in the transistors. The unusual spontaneous ignition of titanium in oxygen helps in melting long pieces of metal and zirconium is used as a fuel in nuclear reactor.

Group (IV) elements beyond the second period have low energy d-orbitals and expand their valence shell by using these orbitals for coordination with Lewis bases. The first member of this group viz., the carbon atom, however, cannot expand its valence shell beyond eight electrons. The s and p sub-group trends, such as an increase with increasing atomic weight, in metallic character of the elements and the stability

of the compounds of the lower oxidation state, are marked in the group.

There are three possible ways in which an element in the IVth group could form compounds: (a) by loss of all four valence electrons to form the M^{4+} ion, (b) by hybridization of the available atomic orbitals in a suitable manner to form four equivalent covalent bonds, and (c) expanding the octet and making use of the empty d-orbitals in a d^2sp^3 hybridization to form adducts with Lewis bases. In the case of tin (IV) compounds one could predict a spherical ion of radius 0.74A^o for ionic bonding, tetrahedral coordination of the tin atom in covalent bonding, and an octahedral coordination in most of the complex ions.

It will be appropriate to give a brief account of some of the important compounds of group (IV) metals and the following paragraphs shall be devoted to this description.

Organometallic compounds of IVth group elements have shown a great biological significance. Organotin compounds have been studied more thoroughly as compared to organosillicon and organogermanium compounds. Organotin compounds have significant use as heat stabilisers for polyvinyl plastics as catalyst in plastic industry, as biocides for antifouling paints, as timber preservatives, as mothproofing agent, as crop protectant and in

certain skin and blood diseases. Ken Walde has shown the antihelminthic and antiprotozoal properties of these compounds in poultry. These compounds have also been used as fungicides and act as strong growth factor for plants. Some other commercial uses of these compounds are, as an oxidant in rubber industry, as an ingredient in certain veterinary medicines, in making electrically conducting film over the surface of glass and as lubricating oil. Dialkyltin compounds have shown a vesicant action and have exhibited lachrymatory properties.

Much of the recent work on group (IV) metal chemistry has concerned the synthesis and characterization of their organometallic compounds (1-4). The position of germanium with reference to other elements in the periodic table is unique, as it represents the mid point in the transition from metallic to nonmetallic properties. Truly speaking it is the crossroad element and its chemical behaviour when compared with its nearest neighbours silicon and tin indicates quite strongly the duality of its nature. Germanium is closer to silicon than to tin and lead in its organic chemistry which is reflected in the higher thermal stability and relatively low reactivity of C-Si and C-Ge bond.

A good deal of work has also been done on the reaction of group (IV) metal halides with various Lewis bases forming donor-acceptor type of complexes often described as adducts,

held together by a coordinate covalent (or dative) bond (5-11). Group (IV) halides act as Lewis acid by accepting a lone pair of electron from a Lewis base. Studies on such addition compounds of group (IV) metal halides particularly those of chlorides are quite extensive.

In the present work, study of the formation and characterization of adducts of halides of group (IV) elements have been undertaken with a view to determining their structure, stereochemistry and comparative Lewis acidity of the halides used. The formation of adducts from tin halides, germanium chloride, silicon chloride, titanium fluoride and titanium chloride, zirconium fluoride and zirconium chloride have been investigated.

Complexes of transition metal ions with various nitrogen containing ligands have been the subject of active research in the past few years (12,13). Adduct formation by the reaction of tin (IV) halides with donor molecules like pyridines, amines, ammonia, anilines, ureas, amides, aminobenzoic acid and anthranilic acid have also been investigated. The corresponding $GeCl_4$ adducts are, in general less stable at room temperature, and have therefore not been well characterised. The formation of 1:2 adduct of $SnCl_4$ with amine and aminobenzoic acid has been confirmed by indicator titration and analytical results (9). Infrared spectra of all these adducts confirmed nitrogen

to metal bonding. The analogous $GeCl_4$ adducts have received little attention, however, its adducts with bipyridyl and terpyridyl have been shown to have a trans-configuration in the solid state, and ionic nature in nitrobenzene (14,15). Trost (16) has studied a trimethylamine adduct of $GeCl_4$ and from the thermal decomposition of this adduct has shown it to be a molecular addition compound. Poller and Toley (17) have studied 4,4'-bipyridyl adducts of stannic chloride and organotin halides of the type R_nSnX_{4-n} where n = 1,2 or 3. Tin (IV) chloride adducts of 4,4'-bipyridyl (1:2) was found to have a trans octahedral geometry. A polymeric structure was suggested for the 1:1 adducts of organotindihalide, and trihalides with 4,4'-bipyridyl. However, a monomeric structure was assigned to 4,4'-bipyridyl triphenyltinchloride adduct. A 1:1 adduct of pyrazine (1,4-diazine) with diphenyltindichloride was also reported but its structure could not be established with certainty.

Germanium tetrahalides as well as organohalogermanes react with amines to form adducts. Most of these, however, are stable only at temperatures below 0^oC. By interaction between $GeCl_4$ and aniline or between $GeCl_4$ and cyclohexylamine, Davidson prepared the compounds $ClGe(NHC_6H_5)_3$, $Cl_2Ge(NHR)_2$ (R = phenyl or cyclohexyl) and $Ge(NHC_6H_{11})_4$ (18). However, generally the derivatives containing two or more $-NH_2$ or -NHR groups bonded

with a germanium atom are unstable. This has been illustrated by the formation of the R_2GeNH and RGeN type derivatives in ammonolysis of organogermanium di-and trihalides, as well as, by the formation of $Ge(NH)_2$ in $GeCl_4$ and GeI_4 ammonolysis (19,20). The $(RHN)_4Ge$ type derivative lead to derivatives of the $Ge(NR)_2$ type. Thomas and Southwood (21) reported the formation of germaium diphenyldiimide dihydrochloride, $Ge(NC_6H_5, HCl)_2$, in the action of $GeCl_4$ on aniline. The action of ethylamine on $GeCl_4$ results in an unstable adduct and finally in the formation of germanium diethyldiimide, $Ge(NC_2H_5)_2$. The action of diothylamine leads to the formation of germanium diethyldiimide hydrochloride, $Ge(NC_2H_5)_2$, HCl. Piperidine, however, yields tetrasubstituted derivatives. The reaction of $GeCl_4$ with monomethylamine results in the formation of a trimeric cyclic molecule, $(Cl_2GeNMe)_3$, having a six-atom backbone of alternating Ge and N atoms (22). Germanium tetrachloride reacts with a number of N,N'-disubstituted ethylenediamines to give spiroimidazolidines with germanium as the central spiro atom (23).

Titanium (IV) chloride forms a cis-octahedral complex with acetylacetonate (24,25). A 2:1 (M:L) adduct of titanium (IV) chloride with succinimide is formed through halide bridging (26). Titanium (IV) chloride is also reported to have formed complexes of trans-configuration with pyridasine (27). Rivest

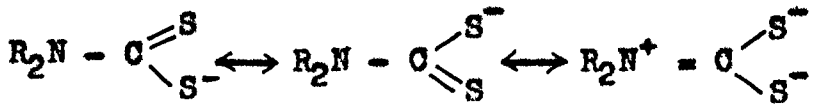
has reported complex formation between titanium (IV) chloride and substituted thiourea with coordination occurring through the nitrogen atom (28). A pentacoordinated titanium (IV) chloride complex has also been reported (28).

A cis-octahedral complex of zirconium (IV) chloride with acetylacetonate has been reported (24,25). Silicon tetraiodide has been found to form a cis-octahedral complex with pyridine in a 1:4 ratio (M:L), whereas, only 1:1 complex is formed with pyridazine (27).

Metal complexes with fluorides of IVth group elements have not been studied in detail owing to the difficulty in handling them. Recent studies have shown that tin (IV) fluoride coordinates with a variety of ligands (29,30). Information of its behaviour towards simple donor molecules is less extensive than for the remaining tin halides. Bidentate ligands like triphenylphosphine oxide and pyridine N-oxide form a binuclear cis-complex with SnF_4. On the basis of stereochemical evidence the structure of this compound was determined by the ligand rather than by the halogen (31).

Metal complexes of dithiocarbamates have been more extensively studied in the past few years (32-34). However, there have been only very limited studies on the complexes of bis-dithiocarbamates. Dithiocarbamates have shown great biological significance (13). A considerable number of sulphur and nitrogen

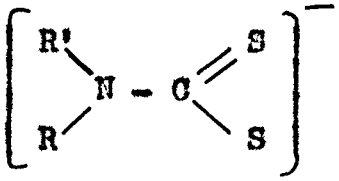
complexes have been used in vitro test system giving a better indication of carcinostatic activity of the compound over a wide range of cancers than other test systems. These compounds are being studied in vivo against leukemia, cancer of lung and melanoma. Halogenonitrophenyl and naphthyl esters of N-substituted dithiocarbamic acids have been found to possess fungicidal activity (35). These have also been used as accelerators in rubber vulcanisation (36). Dithiocarbamates have two coordinating sites viz., nitrogen and sulphur. Sulphur atom in heterocyclic ring has poor coordinating ability since this pseudoaromatic ring has two fold effect of causing the lone pair on sulphur atom to be less available for donation and making π-orbitals less capable of accepting electrons from the metal. Infrared spectral studies on the complexes of metal halides with a number of dithiocarbamates show that the site of bonding is presumably the sulphur atom. The complexing properties of dithiocarbamates are directly connected with the presence of two donor sulphur atoms, which preliminarily determine the nature of metal that can be bonded and the strength of the complexes formed. The structure of the dithio complexes can be represented by the following formulation.



(A) (B) (C)

The extent to which the resonance form (C) contributes to the structure and the effect it has on the physical and chemical properties has been extensively studied. Chatt and coworkers concluded that resonance form (C) does indeed contribute to the structure to a considerable extent (37). The contribution of this structure (C) is greatest for corresponding dialkyl complexes and relatively small for the heterocyclic system, showing less tendency to release electrons to the nitrogen-carbon bond which has as a consequence less double bond character.

In the dithiocarbamate ion R' and R denote various organic substituents which do not influence significantly the metal-sulphur bonding but determine some analytically interesting properties seen with disubstituted dithiocarbamates.



Monosubstituted compounds are less useful because of their reducing properties and tendency to decompose to hydrogen sulphide. The most important property of the dithiocarbamate ion is its protonation in acidic solution and subsequent decomposition to carbon disulphide and protonated amines. Metal dithiocarbamates give characteristic colours which are widely

used for analytical purposes. The colours depend only slightly on the nature of the substituents in the disubstituted dithiocarbamate and may be different for monosubstituted ligand or dithiocarbamates derived from acid amines. It is probably due to the possibility of thiono-thiolo tautomerism or the presence of other reactive donor groups in the ligand molecule. The dithiocarbamates are mostly monomeric, except for copper (I) complexes of diethyl and dipropyl derivatives where tri-and tetrameric structures respectively have been reported (38,39). Glen and Sehwale (40) have indicated that for dithiocarbamate derivatives of diethylamine, piperidine, thiazine, dimethylamine, pyrrolidine, morpholine and piperazine, the ability to stabilize the higher coordination states decrease in the order given. Dithiocarbamates have been reported to coordinate with tetrahalides of group (IV) elements. An octahedral trans-configuration has been proposed for the bis-dimethyldithiocarbamate of tin $[Me_2Sn(SSCNMe_2)_2]$ (41). The configuration of pentacoordinated $Me_2SnX(SSCNMe_2)$ have also been reported (41) (Me = methyl group). Diethyldithiocarbamate forms a chelated and a cis-octahedral complex with tin $[X_2Sn(SSCNEt_2)_2]$ where X = halogen and Et = Ethyl group (42). The morpholine-4-carbodithioate complex of titanium is diamagnetic and eight-coordinated with ligand acting as a bidentate one (43).

There is much less literature on the bis-dithiocarbamate complexes. Polymeric chelates of copper (I) with piperazine bis-dithiocarbamate which contains two CS_2^- groups at the two ends of the heterocyclic ring have been reported (44).

Antipyrine and substituted antipyrine viz., 4-aminoantipyrine are of much interest owing to their biological significance (45). Salts of antipyrine having analgesic and antipyretic properties have recently been investigated. The determination of protonation site in these compounds is of intrinsic interest and of possible metabolic application. In these biologically important salts the tertiary (sp^3) nitrogen atom is protonated in preference to a carbonyl group.

Taking the five-membered pyrazolone ring separately antipyrine is considered as a monosubstituted benzene (46). It has two coordination sites viz., oxygen and nitrogen and is expected to have a unidentate bonding through oxygen, the other behaviour i.e., use of ring nitrogen for coordination is conceivable but unlikely. It contains a carbonyl group which is a potential donor of electron due to large C=O moment. It has a negative potential at the oxygen end of the carbonyl group and is favourable for coordination. The lowering of νC=O of ligand in the complexes shows that the coordination of antipyrine to metal ion is through the carbonyl oxygen (47, 48). The decrease in carbonyl stretching frequency of antipyrine in

complexes is due to the reduction of π-bond character of C=O group on complex formation.

4-Aminoantipyrine (48) has three possible sites of coordination viz., (i) the oxygen of C=O group (ii) the nitrogen of-NH_2 group and (iii) more commonly both the nitrogen and oxygen forming a chelated species. A large number of compounds of antipyrine have been shown to be unidentately bonded and oxygen coordinated. Mostly the complexes of 4-aminoantipyrine (49) involve chelated ligand i.e. the ligand acting as a bidentate. High spin complexes of 4-aminoantipyrine with transition metals viz., Mn(ii), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) have an octahedral geometry with halogen bridging (48). In all these complexes the ligand is chelated. Tetrahedral geometries are encountered with these metals when antipyrine is used.

In recent years quinolines have been found to be biologically active and are used in medicine (50-52). A derivative of benzo (f) quinoline impairs sympathetic transmission by acting on certain inhibitory dopaminergic receptors located on the adrenergic nerve terminals. Its intravenous administration impairs sympathetic nerve response of perfused hind limb, gracius muscle, spleen and nictitating membrane. Derivatives of benzo (f) quinoline are very good antimalarial agents. Natural and synthetic isoquinoline derivatives (aparphine analogue) have moderate antihypertensive activity.

Not much has been done on the complexation of quinoline with group (IV) metal halides and very little is known about their complexes. The quinolines are termed benzo (b) quinoline, benzo (c) quinoline, benzo (g) quinoline, benzo (f) quinoline and benzo (h) quinoline according to the position of nitrogen in the ring. This is the reason why properties of quinolines differ slightly.

Benzo (f) quinoline and benzo (c) quinoline have not been studied thoroughly. In benzo (c) and benzo (f) quinoline nitrogen is a part of heterocyclic system. Benzo (h) quinoline acts as a bidentate ligand coordinating with C-10 and nitrogen (53). Benzo (h) quinoline is unique in the sense that its planarity will not allow the formation of a π-arene complex prior to proton extraction. Thus such an intermediate complex is not a prerequisite in the mechanism of the formation of metal-carbon bond. Dimeric complexes of benzo (h) quinoline are formed with Pt(II) and Rh(III) through a proton abstracting process. The compound with Pd(II) is pentacoordinated dimeric with halogen bridge, while the Pt(II) and Rh(III) complexes are monomeric (53). In some reported complexes of benzo (h) quinoline the σ-bond has been retained. These include compounds in which the bridging chlorines have been exchanged for other anionic ligands, and cationic complexes in which the bridging chlorines have been

exchanged for various neutral ligands. The example of this type of complexation of benzo (h) quinoline is exhibited by complex formation with $PdCl_2$ (53)

A green crystalline binuclear Cu(II) complex with benzo (f) quinoline has been reported. Benzo (f) quinoline and benzo (h) quinoline (54) also form complexes with chromium tricarbonyl. Benzo (c) quinoline forms a complex with gold (55).

CHAPTER - II

EXPERIMENTAL METHODS

EXPERIMENTAL METHODS

Several physico-chemical methods are now available for structure elucidation of coordination compounds. The techniques used for the investigation of the structure of newly synthesized compounds described in the present work are infrared spectroscopy and molar conductance measurements. While informations about these techniques are found in most of the modern text-books, a brief description of these methods seems appropriate.

INFRARED SPECTROSCOPY

Infrared spectrum arises from the different modes of vibrations and rotation of a molecule. The pure rotational spectrum of molecules occurs at very long wave-length in the microwave region well beyond the wave-length limit of about 25μ. At wave-length below 25μ the radiation has sufficient energy to cause changes in the vibrational and of course also the rotational levels of the molecule.

According to quantum theory there are discrete energy states, both rotational and vibrational in which each molecule can exist. For diatomic, linear polyatomic, and spherical top molecules the energy of rotational levels is given by the equation

$$E_r = \frac{J\,(J+1)h^2}{8\,\pi^2 I} \qquad \text{Eqn. (1)}$$

where J is the rotational quantum number which can have any integral value, 0, 1, 2, 3, ..., and I is the moment of inertia of the molecule about the axis of rotation. For symmetrical and asymmetrical molecules the formula is somewhat more complex.

Transitions between the different rotational levels in the microwave and infrared regions are governed by the selection rule $\triangle J = \pm 1$. If a molecule is raised from an energy state with a quantum number J to that with quantum number J+1, the energy involved will be

$$h\nu = \triangle E = E_{J+1} - E_J \qquad \text{Eqn. (2)}$$

from which the frequency of energy absorbed in wave numbers can be obtained by substitution of Eqn. (1) in Eqn. (2) as follows:

$$\nu_r = \frac{h\,(J+1)}{4\,\pi^2 IC} = 2B\,(J+1) \qquad \text{Eqn. (3)}$$

where B, the rotational constant, is equal to $h/8\,\pi^2 IC$. The pure rotational spectrum then would consist of equally spaced lines. The constant frequency separation between successive lines being equal to 2B, i.e., to $h/4\,\pi^2 IC$ cm^{-1}. It will be observed that as the moment of inertia I increases, the frequency of the rotational lines, for a given J value, decreases. For relatively heavy or large molecules, the pure rotation spectrum will thus appear in the very far infrared region.

In the infrared region below 25μ, changes in the vibrational

states of the molecule occur during absorption of radiation for small amplitude of vibration, the vibration may be considered harmonic and the energy of the vibrational quantum level is given by Eqn. (4)

$$E_v = h\omega(v + \tfrac{1}{2}) \qquad \text{Eqn. (4)}$$

where ω is the fundamental vibrational frequency of the harmonic oscillator, and v is the vibrational quantum number which can have any integral value, 0, 1, 2, 3 . . . The difference in energy between successive energy levels of the harmonic oscillator is thus always $h\omega$.

In order that a vibrating molecule should interact with the fluctuating electrical field of electromagnetic radiation the molecular electrical dipole moment must change its magnitude or orientation with respect to a fixed coordinate system during the motion. It is the magnitude of this change of dipole moment which determines the intensity of a transition. There are 3N-6 normal vibrations of a non-linear molecule of N atoms and hence the 3N-6 frequencies associated with them are called fundamental frequencies of the molecule. From the symmetry that a molecule possesses one can determine how many of the 3N-6 vibrations will be observed in its infrared spectrum, and conversely, from the infrared spectrum the molecular symmetry may be deduced. A

vibration will be infrared active if its symmetry species is the same as that of atleast one of the dipole moment components. For harmonic oscillators, transitions between the various energy levels are governed by the selection rule $\triangle v = \pm 1$. In actual fact, the purely harmonic conditions do not prevail for real molecules. The frequent observation of overtones and combination tones of these vibrations corresponding to changes $\triangle v = 2, 3$, etc. is a consequence of the anharmonic nature of the normal modes. These additional bands are usually very much weaker than the parent fundamentals.

For harmonic oscillation the frequency ω is related to the force, f, binding the vibrating groups together and the reduced mass μ, by the relationship

$$2\pi\omega = \left(\frac{f}{\mu}\right)^{1/2}, \quad \mu = \frac{m_A m_B}{m_A + m_B} \qquad \text{Eqn. (5)}$$

where m_A and m_B are the masses attached to either of the vibrating system. In terms of the frequency ν_v, in wave numbers, Eqn. (6) becomes

$$\nu_v = \frac{1}{2\pi C}\sqrt{\frac{f}{\mu}} \qquad \text{Eqn. (6)}$$

Thus the frequencies of vibration of a molecule are related to the masses and binding forces. In many of the normal modes

of vibrations of a molecule the main participants in the vibration are two atoms held together by a chemical bond. The frequencies are only slightly affected by another atom, attached to the atoms concerned, and thus these vibrational modes are characteristic of the group in the molecule and are very useful in identifying a compound, especially in deducing the structure of an unknown substance. In this work, only those frequencies which are pertinent to the discussion of the newly synthesized complexes will be discussed.

N-H Stretching Vibrations - The N-H stretching vibrations occur in the region 3500-3300 cm^{-1} in dilute solutions (56). Primary amines in dilute solutions of non-polar solvents give two absorption bands in this region. The first which is due to symmetric stretch is usually found near 3500 cm^{-1} and the second which arises from the corresponding asymmetrical mode is found near 3400 cm^{-1}. The position and intensity of both these bands are sensitive to substitution. Secondary amines show only a single N-H stretching absorption in dilute solution in the above mentioned region. The intensity and frequency of N-H stretching vibrations of secondary amines are very sensitive to structural changes. The band is found in the range 3350-3310 cm^{-1} (low intensity) in aliphatic secondary amines, and near 3490 cm^{-1} (much higher intensity) in heterocyclic secondary amines such as

pyrrole and indole. Fluorine substitution generally seems to enhance the intensity of the band. Ring strain seems to have little effect on N-H stretching vibration as can be seen by the values of ethyleneimine (3367-3341 cm^{-1}) and dimethylamine (3384 cm^{-1}).

The N-H stretching absorption shifts to lower values in the solid state due to extensive hydrogen bonding. At very low concentration pyrrolidine shows a band at 3367 cm^{-1} due to the monomeric N-H stretching frequency (57). As the concentration increases, a new band appears at 3268 cm^{-1} due to intermolecular association (N-H ... N bonding). The intensity of the low-frequency band increases with increasing concentration until complete association occurs in the liquid state. Hydrogen bonding is very common in ureas and thioureas (58). In concentrated solutions of thioureas in CCl_4 and $CHCl_3$ two to four bands in the 3500-3000 cm^{-1} region are present. The highest frequency band is much sharper than any of the others, the broadness of which can reach 200 cm^{-1}. Further, the molar extinction of the highest frequency band increases with decreasing concentration, the trend being opposite for the other bands. In very dilute solutions only the highest energy band is visible. There is always in the solid spectra, however, a strong, broad band together with weaker and narrower bands on the lower

frequency side. This suggests a strongly associated condition for thioureas in the solid state.

Valuable information has been obtained on the structure and tautomerism of many heterocyclic molecules and their substituted derivatives from a study of the N-H stretching absorption. The α-and γ-mercaptopyrimidines and other mercapto-aza-aromatic compounds exist in the thione form, both in the solid state and in solvents of low polarity (59). In the solid state a weak band in the range 3160-3190 cm^{-1} is regarded as evidence for the presence of -NH group. In solution a broad band is found in the range 3350-3420 cm^{-1}, due to N-H stretching in unassociated molecules (weaker bands also appear at lower frequencies, due to associated molecules). The IR spectra of 2-and 4-hydroxypyrimidines in the solid state and in $CHCl_3$ solution give absorption bands due to N-H bond stretching vibrations, indicating their existence in the tautomeric keto form (60). However, aminopyrimidines, generally, exist in the non-tautomeric form, and in solution ($CHCl_3$,CCl_4) give two bands characteristic of amino group (61, 62).

N-H Deformation Vibrations - For the deformation frequencies of the NH_2 group in primary amines four characteristic peaks should appear, but the only definite assignment has been done in the case of scissoring vibration, generally observed in region 1650-1590 cm^{-1} (63). The lower frequency deformation vibrations

of the $-NH_2$ group have not been investigated in detail. The NH_2 twisting, wagging and torsional vibrations in methylamine have, however, been assigned to 1455, 780 and 264 cm^{-1}, respectively. Secondary aliphatic amines show an extremely weak band in the range 1650-1550 cm^{-1} due to N-H deformation vibration and it is difficult to detect this band readily. The assignment of this vibration is very difficult in the case of aromatic amines because of the presence of aromatic ring vibrations in this region.

C-H Stretching Vibrations - These vibrations are usually observed in the 3100-3000 cm^{-1} region in carbocyclic and heterocyclic systems (57). Some aromatic compounds give rise to three bands near 3038 cm^{-1}. Pyridine shows C-H absorption in the range 3070-3020 cm^{-1} which appear as a series of multiple absorptions under high resolution (64). In pyrimidines this band is observed near 3050 cm^{-1}. A weak band is observed in the case of trisubstituted pyrimidines, since only one free ring hydrogen atom is present. This band is absent in tetrasubstituted pyrimidines.

C-H In-Plane and Out-Of-Plane Deformation Vibrations - A number of characteristic absorption bands in the region 1250-1000 cm^{-1}, exhibited by most of the heterocyclic compounds are attributed to C-H in plane deformation and the ring breathing modes (57). In diazines these bands are observed in the range 1239-1021 cm^{-1} (65). Bands appearing in the region 900-700 cm^{-1} have been attributed

to the C-H out of plane deformation vibrations, and the position of these bands depend on the number of free hydrogen atoms adjacent to one another.

S-H Stretching Vibrations - The S-H vibrations in mercaptans are usually observed in the range 2600-2550 cm^{-1} (66). The S-H absorption is not inherently strong, and is often difficult to detect in dilute solutions or in samples examined in very thin cells. It is also obscured in compounds containing -COOH groups which exhibit general absorption in this region. However, if allowance is made for these factors the presence or absence of a band in this region can afford decisive evidence for the occurrence of a mercapto group.

Simple mercaptans such as propyl, butyl and isoamyl mercaptans give a well defined but rather weak absorption at 2650-2550 cm^{-1}. Randall et al. (67) proposed the range 2688-2560 cm^{-1} for the S-H band, but this is clearly designed to include hydrogen sulphide which has its asymmetric S-H mode at 2688 cm^{-1}. This is an exceptional case, and aromatic mercaptans do not appear to absorb at frequencies higher than 2600 cm^{-1}, Sweeney et al. (68) have shown that 1:2-dimercaptoethane absorbs at 2350 cm^{-1} in the liquid state, but this appears to be wholly exceptional. Thus even thioacetic acid (2550 cm^{-1}) and dithioacetic acid (2481 cm^{-1}) absorb at higher frequencies, indicating that polymerisation does not occur to any extent, and indeed the S-H link is not apparently

capable of the extensive degree of hydrogen bonding which occurs with -OH and -NH groupings. There is very little change in the frequency of S-H absorptions on passing from the liquid state to dilute solutions, so that any intermolecular bonding effects must be very small. On the other hand, small shifts suggestive of hydrogen bonding have been observed in solution in certain bases and other compounds, indicating the formation of weak S-H - - - B bonds. Thiophenol is capable of hydrogen bonding to sulphoxides, to give a frequency shift of the S-H vibration of 100 cm^{-1}, however, with aryl sulphoxides the shift is somewhat smaller.

Studies in this region have been used to determine whether certain heteroaromatic mercapto compounds exist in the mercaptan or thio-keto form (59, 69). The absence of any S-H absorption from the spectrum of mercapto-benzthiazole is one of the strongest pieces of evidence for the existence of this substance as a thio-ketone under normal conditions. 3-Mercaptopyridine and 8-mercaptoquinoline exist in the mercaptan form in solvents of low dielectric constant (59). The broad and weak band at 2520 cm^{-1} in the spectrum of 8-mercaptoquinoline (for which there is no counterpart in the spectrum of 8-methylthioquinoline) is attributed to S-H stretching; there is probably some intermolecular hydrogen bonding between the -SH group and the vicinal nitrogen atom.

C=N Stretching Vibrations - A band of variable intensity in the region 1690-1640 cm^{-1} is attributed to C=N stretching vibrations in open-chain systems or in non-conjugated ring systems (70). With conjugated cyclic systems the position is much less clear, and the C=N absorptions have been assigned as being within the range 1660-1480 cm^{-1}. In cyclic compounds and cyclic materials without internal conjugation the C=N absorption is assigned to the 1650 cm^{-1} region. The C=N absorption band occurs near 1667 cm^{-1} in oxazines, oxazolines, oximes and imines. However, the C=N absorption bands are difficult to identify for two reasons. First owing to the considerable changes in intensity which follow changes in its environment, and secondly because information available on the effects of conjugation in ring systems is often conflicting and indecisive.

C-N Stretching Vibrations - The C-N stretching absorptions give rise to strong bands in the region 1360-1250 cm^{-1} in aromatic amines (56). In aliphatic amines the absorptions are in the 1220-1020 cm^{-1} range and are often of low intrinsic intensity. In aromatic primary amines there is one band in the region 1340-1250 cm^{-1} but in secondary amines two bands have been observed in the region 1350-1280 cm^{-1} and 1280-1230 cm^{-1}. The position of C-N absorption does not differ much from C-C absorption, but the intensity is relatively large because of C-N polarity.

Ring Stretching Vibrations - Characteristic aromatic ring vibrations appear in the region 1600-1350 cm^{-1} (57) in most of the heterocyclic compounds. The position and intensity of these vibrations are dependent on the nature of the ring and type of substitution. Six-membered rings show four bands around 1605, 1575, 1480, and 1430 cm^{-1}, whereas 5-membered rings show three bands around 1590, 1490 and 1400 cm^{-1}. The intensities of these bands give an idea of the pattern and nature of substitution in the ring. Thus, in 4-substituted pyridine-1-oxides and 3-substituted pyridines the intensity of the band around 1605 cm^{-1} is high for both electron-withdrawing and electron-donating substituents, whereas, in the case of 2- and 4-substituted pyridines and 3-substituted pyridine-1-oxides, the intensity is high with electron donor groups and low with electron acceptor groups. The intensity of the band at around 1575 cm^{-1} also shows similar variations with substitution. Electron donating substituents increase the intensity of the band at around 1480 cm^{-1}, whereas the band near 1430 cm^{-1} is unaffected by the nature of the substituents. This particular trend in the change of intensities has been explained as being due to the charge disturbances in the molecule.

The characteristic pattern of absorption of the ring stretching vibrations results from the complete interaction of the C=C, C=N and/or N=N vibrations (e.g., in 1,2-diazine) and it

is, therefore, very difficult to isolate the different vibrations. This is due to the fact that the lone pair of electrons on the nitrogen atom will be able to conjugate with the ring, the magnitude of which depends on the coplanarity of the system. therefore, these vibrations are sensitive to minor alterations in molecular geometry and are difficult to distinguish from other vibrations. Even though a band of variable intensity in the region 1660-1630 cm^{-1} is attributed to C=N stretching in open-chain α, β-unsaturated compounds, in cyclic conjugated systems the appearance of bands in this region can only be attributed to the ring stretching modes.

Substituted pyrimidines, generally, show four bands in the 1590-1375 cm^{-1} region (65, 71-73). The aminopyrimidines show a band at about 1650 cm^{-1} (64) which is probably due to NH_2 deformation mode. The hydroxypyrimidines are also not suitable for the development of correlations for ring vibrations of this type, as they may exist in the tautomeric keto form, in which the double bond absorptions of the ring would be expected to be different from the fully aromatic systems.

<u>C=O Stretching Vibrations</u> - The C=O stretching vibrations of various carbonyl groups absorb in the region 1900-1600 cm^{-1} (74). A more specific range is defined by the type of carbonyl (e.g., ketones, esters, etc.), and the position is further affected by a variety of effects. The frequency of the carbonyl absorption is

determined almost wholly by the nature of its immediate evnironment, and the structure of the rest of the molecule is of little importance unless it is such as to give rise to chelation or some similar effect. Thus the carbonyl frequency shifts away from the normal position in α β-unsaturated materials and in carbonyl compounds with strongly electronegative substituents on the α-carbon atom, whilst in cyclic ketones the frequency shift and its direction are related to the degree of strain of the ring. Frequency shifts due to chelation and to mutual interference effects can also be considerable in some cases. However, in each of these cases the extent of the frequency shift to be expected is known, and the new range of frequencies falls within comparatively narrow limits.

A carbonyl group situated between two methylene groups represents the simplest case of an undisturbed C=O stretching vibration. Studies by many workers have shown that in solution the frequency of the carbonyl absorption of simple ketones of this type always lies within the narrow range 1725-1706 cm^{-1}, provided that no hydrogen bonding or other interference effects occur (75). Carbonyl groups in unstrained saturated rings absorb within the same overall frequency range 1720-1706 cm^{-1}.

The physical state has a direct effect on the carbonyl frequency. Acetone, for example, absorbs at 1742 cm^{-1} in the vapour phase, whereas in solution the frequency lies between

1728 cm^{-1} and 1718 cm^{-1}, depending on the solvent. Similarly, dodecyl ketone absorbs at 1740 cm^{-1} in the vapour state, and between 1724 cm^{-1} and 1717 cm^{-1} in solution. It is probable that some form of dipolar association is occurring in the condensed phase, resulting in a low frequency shift of the order of 20 cm^{-1}.

Conjugation of a carbonyl group with a C=C linkage results in a lowering of the frequency by an amount depending on the nature of the double bond. An aliphatic C=C bond in conjugation with a carbonyl group reduces its frequency by about 40 cm^{-1} and the absorption occur in the range 1685-1665 cm^{-1}. When an aryl group is directly attached to the carbon atom of a carbonyl group, the frequency shift of the carbonyl is less than that occurring with a full double bond in conjugation, and the absorption band occurs in the range 1700-1680 cm^{-1}. With two aryl groups directly attached, however, there is a further fall in the frequency to 1670-1660 cm^{-1}. The influence of an α-aryl group is additive with that of any other structure which is capable of influencing the C=O frequency. With a six-membered ring C=O with an α-aryl group, the frequency is found to be 1695-1686 cm^{-1}, which is the same as with similar open-chain materials. With a five-membered ring C=O, however, the frequency increases to 1715-1706 cm^{-1}, the strain of the five-membered ring being offset to some extent by the aromatic conjugation. Halogen substitution in the immediate vicinity of carbonyl group results in a high frequency shift of the carbonyl absorption. This is particularly marked in the acid

chlorides, where a chlorine is directly attached to the carbonyl group, but there is still an appreciable effect when the halogen is situated on the α-carbon atom. Thus α-chloropropionic acid, for example, absorbs at 1730 cm^{-1}, as against 1710 cm^{-1} for β-chloropropionic acid.

When intramolecular hydrogen bonds are formed, the carbonyl absorption bands may be lowered by 50 cm^{-1} according to H-bond strength (74). 1-Hydroxyanthraquinone shows two C=O bands at 1680-1675 cm^{-1} and 1630-1622 cm^{-1}, corresponding to free and bonded carbonyl groups. With two hydroxyl groups in each of the β-positions only one band is shown at 1639-1623 cm^{-1}, whilst in the extreme case of 1, 4, 5, 8-tetrahydroxyanthraquinone the carbonyl frequency has fallen to 1595 cm^{-1}. Similarly fumaric acid absorbs at 1680 cm^{-1}, in contrast to the normal value of 1705 cm^{-1} of maleic acid. Salicyclic acid absorbs at 1655 cm^{-1} which is comparable with the shifts experienced in the case of the α-hydroxy-αβ-unsaturated ketones. 3-Amino-2-naphthoic acid absorbs at 1665 cm^{-1}.

All amides show a strong absorption band near 1640 cm^{-1} when examined in the solid state (75). The fact that the absorption is at an appreciably lower frequency than the carbonyl absorption of normal ketones, must be due to the effect of resonance with the ionic form. This is enhanced by the strong association effects in the solid state, and the corresponding vapours absorb at considerably higher frequencies. The amide I absorption is subject

to a considerable alteration on change of state in which hydrogen bonding is broken, and is also liable to variations in solution depending on the polarity of the solvent employed. Thus hexoamide absorbs at 1655 cm^{-1} in the solid state, at 1668 cm^{-1} in concentrated solutions and at 1680 cm^{-1} in dilute chloroform solution. The corresponding values of 1692 cm^{-1} and 1672 cm^{-1} given for this absorption band in dioxane and in methanol indicate the degree of frequency shifts likely to be associated with alteration in the type of solvent employed. The carbonyl absorption of N-ethyl-acetamide ranges from 1687 cm^{-1} to 1663 cm^{-1} over a series of solvents, even at concentrations at which hydrogen bonding effects are precluded. At higher concentrations the frequency varies continuously with the concentration due to change in strengths of the intermolecular hydrogen bonds. Formamide absorbs at 1740 cm^{-1} as vapour and at 1709 cm^{-1} in dilute chloroform solution. Thus, the vapour carbonyl frequencies are much closer to those of ketones and suggest that the contribution of the ionic form is quite small under these conditions.

N, N-Disubstituted amides are incapable of forming hydrogen bonds, and the carbonyl absorption band is consequently not much influenced by changes in physical state. In these cases the amide I band usually falls near 1650 cm^{-1} unless a phenyl group is substituted on the nitrogen atom, when it is raised to 1690 cm^{-1}. This is due to the competitive effect of the ring for the lone pair electrons of the nitrogen atom. In consequence the contribution of the ionic form of the amide is reduced and the carbonyl frequency

is raised. A similar effect may account for the high frequencies shown by N-nitrosoamides, which absorb near 1740 cm^{-1} in solution. The inverse effect occurs in dimethylurea, in which the ionic character of the carbonyl is reinforced by the second nitrogen atom so that in the solid state the frequency falls to 1610 cm^{-1}.

Infrared spectral work (73, 76-82) has shown that a large number of α-and γ-hydroxy-aza-aromatic derivatives are amides both in solid state and in solution. A very strong band in the range 1620-1750 cm^{-1} shows the presence of a-CO group. 2-Hydroxypyrimidine and the 4-isomer in the solid state and in solution show absorption bands in the 1600-1700 cm^{-1} region which have no counterpart in the spectra of the methoxy derivatives and must be due to the C=O bond stretching vibrations. Thus these compounds in the states examined exist predominantly in the amide form.

C=S Stretching Vibrations - The identification of the position of the C=S absorption has been a matter of some difficulty. In carbon disulphide the C=S stretching modes have been assigned to 1522 cm^{-1} and 650 cm^{-1}, whilst in carbonyl sulphide it is given at 859 cm^{-1} (66). These are unusual cases in which the carbon is doubly unsaturated, and they do not offer any guidance to the likely position of the C=S vibration in saturated thioesters and similar compounds. Preliminary calculations indicated that the ratio C=O/C=S would be about 1.5 and that the C=S frequency would

be found in the 1200-1050 cm^{-1} region. Just as is the case with the carbonyl group, the C=S absorption is found to be sensitive to the nature of the surrounding structure but the relative effects of various substituents are not always the same, and the ratio between the carbonyl and thiocarbonyl frequencies varies over the range 1.6-1.14.

Systematic correlations of the available data on thiocarbonyl stretching frequency indicate that when it is unambiguously identifiable, e.g., in $(-CH=CH-)_2$ C=S and -CS.SR derivatives, it is at 1150 $\pm$ 70 cm^{-1} (83, 84). However, in some molecules, notably thioamides and thioureas the thiocarbonyl stretching frequency is uncertain, as there is complete mixing (85, 86) between the C=S stretching motion and other vibrations of similar frequencies. This frequency is hardly susceptible to polar effects. It has been calculated (87) that the C=S stretching frequency in thioformaldehyde should be 1120 $\pm$ 40 cm^{-1}, while in thiocarbonyl chloride it is at 1140 cm^{-1}. By contrast, the carbonyl stretching frequency in carbonyl chloride (1827 cm^{-1}) is considerably higher than that in formaldehyde (1744 cm^{-1}). Presence of thiocarbonyl stretching frequency in mercapto compounds, provides a direct evidence for their existence in the thioamide form. Spinner (59) observed an intense band in the range 1100-1190 cm^{-1}, in several α-and γ-mercaptoase-aromatic compounds, attributable to C=S stretching frequency indicating them to be in the thioamide form.

There has been great indefiniteness with regard to the assignment of the C=S stretching frequency in nitrogen containing compounds and the assignments in these compounds vary in the wide range of 850-1570 cm^{-1} (88). Elmore (89) has shown that the band which is generally assigned to C=S stretching vibration in such compounds results from the coupling of the C-N and C=S stretching vibrations. Normal coordinate analysis of N-methylthioformamide, N-methylthioacetamide, N,N'-dimethylthiourea and tetramethylthiourea (90, 91) shows clear evidence for vibrational mixing in these compounds. In secondary thioamides the bands with considerable contribution from the C=S stretching vibration are found in the region 870-700 cm^{-1} (92).

This is considerably lower than in simple thiocarbonyl compounds where the C=S vibration is localised. In thiourea, two bands in the region 1080-730 cm^{-1} are found to have appreciable contribution from the C=S stretching vibration (85). Suzuki's calculations (91) show that the 843 cm^{-1} band for $HCSNH_2$ correspond to an almost pure C=S mode and the intrinsic frequency of the C=S vibrations vary in the region from 900 to 850 cm^{-1}. Gosavi et al., (90) performed a normal coordinate analysis of N,N'-dimethylthiourea and tetramethylthiourea and assigned various mixed C=S stretching frequency bands. The mixed vibration bands of N,N'-dimethylthiourea have the contribution from C=S stretching vibrations as: 1504 cm^{-1}, 10%; 1420 cm^{-1}, 18% and 752 cm^{-1}, 83%. Similarly in tetramethylthiourea the contribution from C=S stretching vibrations is as:

1408 cm^{-1}, 25%; 1013 cm^{-1}, 50%; 990 cm^{-1} 50% and 462 cm^{-1}, 37%. Since the force constants f_{CN} and f_{CS} are quite similar, the major contributions from C-N and C=S vibrations are found in the bands which are quite close to each other (e.g., 850 and 752 cm^{-1} in N-N'-dimethylthiourea). The mixed vibration bands are in the regions of so-called >N-C=S bands (92).

Metal-halogen Vibrations - Metal halogen vibrations which appear in the low-frequency infrared region, are quite useful in determining the stereochemistry of coordination compounds. In a tetrahedral MX_4 molecule (Td) there are four normal modes of vibration. All the four vibrations are Raman active, whereas only two (ν_3, ν_4) are infrared active, and their position depends upon the mass of the metal and halogen (93). For an octahedral MX_6 molecule (O_h) (e.g., $GeCl_6^{-2}$, $SnCl_6^{-2}$, etc.) there are six possible normal modes of vibration. Three (ν_1, ν_2 and ν_5) are Raman active whereas, only two (ν_3, ν_4) are infrared active (94). In octahedral ions (GeX_6^{-2}, SnX_6^{-2}, etc.) the M-X vibrations are found at lower frequencies than those found for similar vibrations in a tetrahedral environment. When metal tetrahalides, MX_4, form octahedral complexes, $MX_4 \cdot 2$ donor, the M-X stretching vibrations by analogy with these octahedral ions, are considerably shifted to lower frequencies (9, 12, 95-97) relative of those of the free tetrahalides. In many addition compounds metal-halogen vibrations are much more intense than ligand

vibrations. In group IV, this is most marked for adducts of tin tetrahalides and least marked for adducts of silicon tetrahalides where intensities are frequently comparable.

Ligands may occupy either cis- or trans-positions in the octahedron. The use of infrared spectroscopy in the far IR region to study the cis-trans isomerism of the adducts of the type MX_4L_2 (where M is silicon, germanium, or tin, X is halogen and L is a monodentate ligand) has been outlined by many workers (97-104). Neglecting the coupling between the M-X and the ligand vibration, the trans-adduct is considered to be similar to a perturbed square planar MX_4 unit, so that only one infrared active fundamental M-X stretching vibration (e_u symmetry) is predicted, however, for the cis-configuration there would be atleast two fundamentals (97). There are numerous flaws in this simple approach. Fermi resonance may make a combination band intense enough to be accepted as a fundamental. Alternatively, certain fundamentals may be very weak, as for gaseous antimony trichloride, whose a_1 fundamental is very strong relative to the weak e fundamental. Accidental degeneracies may occur or bands may be unresolved. Electronic transitions and lattice vibrations may appear. Calcium fluoride, for example, has a broad infrared absorption band at about 270 cm^{-1}. Crystal-field effects may resolve degeneracies, thus one triply degenerate f_{1u} fundamental of symmetrical SiF_6^{-2} is resolved into two peaks in the crystalline compound $BaSiF_6$, probably owing to elongation of the

octahedron along the three-fold axis, causing a lowering of the symmetry from O_h to D_{3d}.

Beattie and coworkers (105) carried out a normal coordinate analysis of the octahedral species cis-and trans-MX_4L_2 by Wilson's F-G matrix method, and calculated vibrational frequencies for coordination compounds of some tetrahalides of Group (IV). The calculations show that for a cis-adduct three high frequency bands are to be expected, the next nearest band lying considerably below this group (all the bands are infrared and Raman active). In the case of the trans-adducts if the metal-ligand force constant is low compared with the metal-halogen, there will be one main band in the same region as the set of three absorptions mentioned for the cis-adducts. However, where the metal-ligand force constant is high, the e_u and a_{2u} vibrations (both IR active) will occur in similar regions of the spectrum. Thus, in a crystalline compound, crystal-field resolution of the e_u vibration to a doublet, plus the presence of an a_{2u} vibration could lead to a spectrum similar to that of a cis-adduct. The e_u vibration (antisymmetric stretch) is relatively insensitive to the value of f_{M-L} and also to the value of the bending force constants. Thus, identification of cis-and trans-isomers by infrared spectroscopic examination is helpful in favourable cases, particularly when solution spectra can be obtained.

Metal-ligand Vibrations - The metal-ligand stretching frequency is of particular interest since it provides direct information

regarding the coordinate bond. It appears in the low-frequency region and depends on the following factors.

1. Mass of the metal and ligand
2. Oxidation number of metal ion
3. Coordination number of metal ion
4. Geometry of the complex
5. Basicity of the ligand molecule
6. Bridging or non-bridging anions
7. Ligand-field stabilization energy.

MOLAR CONDUCTANCE

The conductivity measurement is one of the simplest and easily available techniques used in a research laboratory, for the characterization of coordination compounds. It gives direct information regarding whether a given complex is ionic or covalent, i.e., whether the anions satisfy the primary or the secondary valency of the metal ion in a coordination compound. Several studies of molar conductivities (106-118) of different kind of electrolytes in different solvents are now available and it is useful to compare molar conductance (Λ_m) value of a given complex with that of the similar electrolyte. Conventionally solution of 10^{-3}M strength are used for the conductance measurement. Molar conductance values for different type of electrolytes in nitrobenzene at this concentration are as 1:1, 20-30; 2:1, 50-60; 3:1, 70-82; 4:1, 90-100 ohm^{-1} $cm^2 mole^{-1}$ (114).

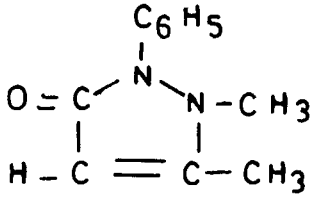
A good description of electrolytic behaviour of coordination compounds in various organic solvents is given in a recent review (114). Molar conductance values for complexes of the various electrolyte types at 10^{-3}M concentrations in nitromethane are as 1:1, 75-95; 2:1, 150-180; 3:1, 220-260; 4:1, 290-330 $ohm^{-1}cm^2$ $mole^{-1}$. Reference values for non-complex electrolytes lead to an average Λ_m value for 1:1 electrolytes of $\sim$91.5 $ohm^{-1}cm^2mole^{-1}$. However, the values for the tetraphenylborate and tetraisoamylborate salts are very low because of the low ionic mobilities, and if these values are excluded from the overall average, a value of $\sim$96 $ohm^{-1}cm^2mole^{-1}$ is obtained. Average values for complexes of unidentate ligands are for 1:1 electrolytes 88.5 $ohm^{-1}cm^2mole^{-1}$ and for 2:1 electrolytes 167 $ohm^{-1}cm^2mole^{-1}$. For the whole range of complexes which has been studied, values claimed for 1:1 electrolytes range from 60-115 $ohm^{-1}cm^2mole^{-1}$, with an average value of $\sim$83 $ohm^{-1}cm^2mole^{-1}$. For 2:1 electrolytes, values claimed cover the range 115-250 $ohm^{-1}cm^2mole^{-1}$, an average value being 168 $ohm^{-1}cm^2mole^{-1}$. Values as low as 180 $ohm^{-1}cm^2mole^{-1}$ and as high as 300 $ohm^{-1}cm^2mole^{-1}$ have been given for 3:1 electrolytes. A reasonable average value is 242 $ohm^{-1}cm^2mole^{-1}$. For 4:1 electrolytes (115-118), values cover a range 244-341 $ohm^{-1}cm^2mole^{-1}$ with an average value of 307 $ohm^{-1}cm^2mole^{-1}$. An unusual electrolyte type is the compound $\left[CrL_3\right]_2(SO_4)_3$, where L = 2-aminoethylpyridine, for which a value of 419 $ohm^{-1}cm^2mole^{-1}$ is quoted.

CHAPTER - III

COMPLEXES OF GROUP (IV) METAL HALIDES WITH PYRAZOLONES

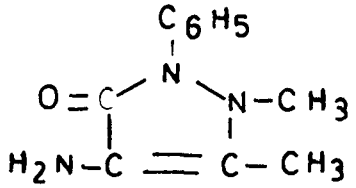
COMPLEXES OF GROUP (IV) METAL HALIDES WITH PYRAZOLONES

1-Phenyl-2, 3-dimethyl-5-pyrasolone (antipyrine, phenazone) (Fig. I) has been found to be unidentate and oxygen coordinated in a large number of its metal complexes (48, 119, 120), however, in mercury cyanide complex, $2Hg(CN)_2$ (antipyrine), it behaves as a bidentate ligand coordinating through oxygen and the ring nitrogen (121). 4-Aminoantipyrine (Fig. II) is known to act as a chelating bidentate ligand, coordinating through oxygen and amino-nitrogen (48). Although some complexes of antipyrine and 4-aminoantipyrine with Ti(III), Ti(IV) and Sn(IV) have been reported earlier (122-124), no structural investigations have so far been carried out. It was, therefore, worthwhile synthesizing and studying the complexes of antipyrine (ap) and 4-aminoantipyrine (aap) with germanium (IV), tin (IV), titanium (IV) and zirconium (IV) halides.



Antipyrine

Fig. I



4-aminoantipyrine

Fig. II

EXPERIMENTAL

PREPARATION AND PURIFICATION OF REAGENTS

Preparation of tin (IV) chloride

Anhydrous stannic chloride was prepared according to standard method (125). Thionyl chloride was added to $SnCl_4.5H_2O$ (May and Baker) in a flask with ground glass joints and the mixture was refluxed for a few hours with a drying tube attached to the condenser. The excess thionyl chloride and hydrogen chloride formed during the course of reaction were removed by distilling over a water bath. Sulphur dioxide was removed by evacuation and crude $SnCl_4$ was left in the reaction flask which was then distilled at 114°C. The first and the last fraction of the distillate were rejected to ensure complete removal of thionyl chloride and sulphur dioxide. Owing to its hygroscopic nature it was stored in a closed vessel having a tightly fitting stopper. The following equation represents the reaction.

$$SnCl_4.5H_2O + 5SOCl_2 = SnCl_4 + 5SO_2 + 10HCl$$

Preparation of anhydrous tin (IV) bromide

Pieces of tin metal were taken in a long neck distilling flask with a side arm close to the body of the flask having calcium chloride tube (125). The flask was closed with a single hole rubber stopper and a dropping funnel with its tube drawn

out to a capillary, so inserted into it that it nearly touched the bottom. Pure bromine was then added dropwise through the funnel. Addition of bromine produced a vigorous reaction accompanied by the evolution of heat. Addition of bromine was so regulated that the temperature did not exceed the boiling point of bromine, i.e., 59°C, and no $SnBr_4$ therefore, or bromine were allowed to penetrate into the side arm. This was conveniently achieved by cooling the reaction flask in ice after each addition of bromine. When the reaction was completed the dropping funnel was replaced by the thermometer and the side arm was kept upward and the flask was heated to remove the excess of bromine, whereas, $SnBr_4$ condensed in the flask. When the product became nearly colourless it was distilled taking care to keep atmospheric air out. After cooling snow white crystalline substance was obtained. Further purification was done by fractional distillation. It is a highly hygroscopic substance, so it was stored in a glass container having tightly fitting stopper.

$$Sn + 2Br_2 = SnBr_4$$

Preparation of tin (IV) iodide

It was prepared by the action of iodine over powdered tin in carbon disulphide (125). Tin powder was prepared by melting tin and grinding it in a mortar when hot. Six parts by weight of pure CS_2 were poured over one part by weight of tin powder in a round bottom flask with a ground glass stopper, and 4 parts by

weight of iodine were gradually added. This reaction flask was kept cooled with ice till the addition of iodine was complete. A red brown liquid was formed which was then transferred to another flask and evaporated to dryness by an aspirator vacuum. The attached side arm of the flask was connected to calcium chloride tube to prevent moisture. Tin (IV) iodide thus obtained was further purified by recrystallisation from chloroform. After recrystallisation orange-red crystalline substance was obtained.

$$Sn + 2I_2 = SnI_4$$

Preparation and Standardisation of Stock Solution of Metal Halides

Anhydrous metal halide ($SnCl_4$, $SnBr_4$) was transferred to a 100 ml volumetric flask. The volume was made upto the mark by absolute ethanol or chloroform, and 10 ml of this solution was taken in a beaker and hydrolysed by addition of hot distilled water with continuous stirring (126). The contents were then heated on a water bath and the precipitate allowed to settle. It was cooled, filtered through the gravimetric filter paper, Whatman 42, and thoroughly washed with hot water to ensure complete removal of hydrochloric acid. The precipitate was dried and ignited in a previously weighed silica crucible, when a white substance was left which was weighed as SnO_2.

$$SnCl_4 + 4H_2O = Sn(OH)_4 + 4HCl$$

$$Sn(OH)_4 = SnO_2 + 2H_2O$$

From this weight of SnO_2 the amount of $SnCl_4$ or $SnBr_4$ was calculated in 10 ml solution. Thus the strength of the stock solution was determined and further dilution was made by taking portions from this stock solution. Solution of tin (IV) iodide was prepared directly from its crystals as it does not hydrolyse in air. Germanium tetrachloride (Koch-Light) solution was standardised by estimation of the germanium in the solution by tannin procedure (127). Anhydrous titanium tetrachloride (BDH reagent) was standardised by hydrolysing it with 10% HCl and weighing the dried precipitate as TiO_2 from this weight of TiO_2 the amount of $TiCl_4$ was calculated in the solution. The solution of desired concentration was prepared in absolute alcohol.

Zirconium tetrachloride (BDH reagent) was used as such. Solution of zirconium tetrachloride was taken in absolute alcohol when required. 4-Aminoantipyrine (M.P 108°C), antipyrine (M.P 113°C) (both Koch-Light reagents) were used without further purification.

All the manipulations were carried out in a dry box in an atmosphere of dry nitrogen.

Techniques Used

Elemental analysis for carbon, hydrogen and nitrogen were done on a Coleman analyser in the microanalytical laboratory in the Chemistry Department at Aligarh Muslim University, Aligarh.

The estimations of halogens and metals were done gravimetrically. In tin complexes metal was estimated as SnO_2 by decomposing the complex with HCl and HNO_3 and then heating it to redness. From the weight of SnO_2 the amount of Sn was calculated. Titanium and zirconium were estimated from their respective complexes as their oxides (128) from which the percentage of metal was calculated. Halogen estimation was carried out by fusing a known amount of complex with fusing mixture (KNO_3 and K_2CO_3). The molar conductance of the complexes at room temperature was determined at 10^{-3}M concentration in nitrobenzene using a systronix conductivity bridge type 302.

Infrared and far infrared spectra were recorded in nujol mull on a Perkin Elmer 621 spectrophotometer in the instrumentation center, Department of Chemistry, A.M.U., Aligarh.

PREPARATION OF THE COMPLEXES

Tetrachloro-(4-aminoantipyrine) tin (IV) $[SnCl_4(aap)]$: An alcoholic solution of tin (IV) chloride and the stoichiometric amount of 4-aminoantipyrine in 1:1 ratio was taken. Metal chloride solution was added slowly to the saturated ligand solution, when a buff coloured precipitate was obtained immediately. It was filtered after a few hours and washed with absolute alcohol and dried in a vacuum desiccator.

Tetrabromo-(4-aminoantipyrine) tin (IV) $[SnBr_4(aap)]$: This red coloured complex was also prepared in the manner described above

by taking a 1:1 (metal bromide: ligand) ratio. It was also dried in vacuum over phosphorous pentaoxide.

Tetraiodo-(4-aminoantipyrine) tin (IV) $[SnI_4(aap)]$: Tin (IV) iodide was dissolved in chloroform. On vigorous mixing of metal iodide solution to ligand solution in 1M:1L ratio, dark-red coloured precipitate appeared at once which was washed with chloroform and dried in vacuum.

Tetrachloro bis-(4-aminoantipyrine) germanium (IV) $[GeCl_4(aap)_2]$: Germanium (IV) chloride solution was taken in dry chloroform. Stoichiometric amounts of $GeCl_4$ and 4-aminoantipyrine were mixed. After keeping the mixture for a few hours a brown coloured complex appeared. It was also dried like other complexes.

Tetrachloro bis-(4-aminoantipyrine) titanium (IV) $[TiCl_4(aap)_2]$: Anhydrous solution of titanium (IV) chloride was taken in absolute alcohol. On mixing metal chloride and ligand solutions in stoichiometric amounts which were taken in the same solvent, nothing appeared at once but after keeping for a few hours a brown coloured complex appeared which was dried in vacuum over phosphorous pentaoxide.

Tetrachloro bis-(4-aminoantipyrine) zirconium (IV) $[ZrCl_4(aap)_2]$: Alcoholic solutions of zirconium (IV) chloride and ligand in (1:2) ratio, after vigorous shaking gave a brown coloured

precipitate which was washed with the solvent and dried in vacuum.

Tetrabromo bis-(antipyrine) tin (IV) $[SnBr_4(ap)_2]$: Solutions of metal bromide and ligand in 1M:2L ratio, in alcohol on mixing gave a light-yellow coloured complex which was washed and dried in vacuum.

Tetraiodo bis-(antipyrine) tin (IV) $[SnI_4(ap)_2]$: Mixing of two chloroform solutions viz., of metal iodide and ligand in 1:2 ratio gave a dark-brown coloured precipitate which was washed with chloroform and dried by usual method of vacuum drying.

Tetrachloro bis-(antipyrine) germanium (IV) $[GeCl_4(ap)_2]$: Stoichiometric amounts of germanium (IV) chloride and ligand were taken in chloroform. Mixing of the two solutions gave a white coloured complex which was washed with chloroform and dried in vacuum.

Tetrachloro bis-(antipyrine) zirconium (IV) $[ZrCl_4(ap)_2]$: Zirconium tetrachloride was dissolved in cold absolute alcohol. This solution was added slowly to a solution of the ligand in 1M:2L ratio. A yellow coloured complex appeared which was washed with alcohol and dried in vacuum.

RESULTS AND DISCUSSION

The analytical data (Table 1) indicates that tetrachloro, tetrabromo and tetraiodo tin (IV) complexes of 4-aminoantipyrine are in 1:1 metal halide to ligand ratio. Tetrachloro germanium (IV), zirconium (IV) and titanium (IV) complexes of 4-amino-antipyrine are of the type $MCl_4.2L$. All the antipyrine complexes which we have prepared viz., tetrabromo and tetraiodo tin (IV) and tetrachloro germanium (IV) and zirconium (IV) complexes are of the type $MX_4.2L$. They are fairly stable at room temperature. The molar conductance of 10^{-3}M solutions of the complexes, which were soluble in nitrobenzene, have been measured at room temperature to see if they were ionised. It has been observed that these values fall well below (Table 1) those quoted for typical uni-univalent electrolytes in this solvent. This indicates that the complexes are basically non ionic, the slight conductivity being due either to some solvation of the type $SnX_4.2L + Solvent \rightleftharpoons (SnX_5(Solvent)L_2)^+ X^-$ or to slight hydrolysis due to handling difficulties of such low concentrations of moisture sensitive solvents.

There are two coordinating sites in antipyrine viz., the oxygen and the nitrogen atoms of the ring. Antipyrine is expected to be unidentate, bonding through the oxygen atom only, although the use of ring nitrogen is conceivable but unlikely.

TABLE - 1

Color, melting point, analytical data and molar conductance* of the complexes

Complexes	Colour	M.P. (°C)	% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% X Found (Calcd)	% Metal Found (Calcd)	Λ_m Ohm^{-1} cm^2 $mole^{-1}$
$SnCl_4(aap)$	Buff	278	28.30 (28.48)	3.11 (2.82)	9.40 (9.06)	29.60 (30.56)	24.81 (25.65)	1.62
$SnBr_4(aap)$	Red	260	19.86 (20.59)	2.50 (2.04)	6.10 (6.55)	50.74 (49.82)	17.28 (18.47)	1.80
$SnI_4(aap)$	Dark-Red	235	16.10 (15.92)	1.30 (1.58)	5.80 (5.06)	61.99 (61.17)	14.81 (14.29)	2.01
$GeCl_4(aap)_2$	Brown	195	43.20 (42.55)	4.80 (4.22)	12.80 (13.54)	23.04 (22.78)		
$TiCl_4(aap)_2$	Brown	210	44.90 (44.32)	4.51 (4.39)	14.80 (14.10)	22.69 (23.78)	8.30 (8.08)	
$ZrCl_4(aap)_2$	Brown	230	41.81 (41.31)	4.50 (4.10)	12.70 (13.14)	21.99 (22.17)	13.81 (14.33)	
$SnBr_4(ap)_2$	Light-Yellow	150	31.54 (32.45)	3.09 (2.97)	7.02 (6.88)	40.81 (39.22)	14.21 (14.44)	1.28
$SnI_4(ap)_2$	Dark-Brown	260D	25.70 (26.37)	1.99 (2.41)	5.90 (5.59)	49.82 (50.66)	10.15 (11.81)	1.60
$GeCl_4(ap)_2$	White	240D	45.10 (44.71)	3.90 (4.09)	8.60 (9.48)	24.55 (23.99)		
$ZrCl_4(ap)_2$	Yellow	60	43.30 (43.34)	4.32 (3.97)	9.20 (9.19)	22.48 (23.26)	13.71 (14.93)	

* Λ_m of 10^{-3}M solution in nirobenzene at room temperature

D = decomposition temperature

A large number of compounds of this ligand have been shown to be unidentate and oxygen coordinated from infrared spectral studies (47). A variety of coordination geometries are encountered. Antipyrine molecule has a negative potential at the oxygen end of the carbonyl group and is favourable for coordination. A strong band reported at 1666 cm^{-1} in the free antipyrine which is assigned to ν(C=O) stretching is observed at lower frequency in the complexes indicating that antipyrine is coordinated through the carbonyl oxygen, thereby decreasing the bond order and stretching frequency of C=O bond.

The spectrum of antipyrine is quite complex to make definite assignments. However, considering antipyrine as a monosubstituted benzene and taking the five-membered pyrazone ring separately, the strong bands at 1582 and 1505 cm^{-1} are assigned to the ring stretching of pyrazolone in antipyrine. Five-membered heteroaromatic compounds are found to give two strong bands at approximately 1590 and 1490 cm^{-1} which are considered to be characteristic of the five-membered ring (129, 130). The bands assigned to the vibrations of the benzene ring compare well with those of monosubstituted derivative of benzene (131). The ring stretching vibrations probably result from the complete interaction of ν (C=N) vibrations (Table 2) and it is therefore very difficult to separately isolate the different vibrations. The ring stretching vibrations in complexes of ap and aap are

TABLE - 2

Assignments of IR spectra (4000-200 cm^{-1}) of ligands and complexes

Compound	Assignments					
	ν (N-H)	ring vibrations		ν(C=O)	ν(M-O)	ν(M-X)
asp	3435m, 3330m	1600vs	1500vs	1650vs		
$SnCl_4(asp)$	3300w, 3225w,b	1600vs	1515sh	1550vs	488m	330vs
$SnBr_4(asp)$	3225sh, 3185m	1600w	1515sh	1555vs	470s	240s
$SnI_4(asp)$	3180w,b	1595sh	1538vs	1580vs	450s	**
$GeCl_4(asp)_2$	3430m, 3340m	1615w	1525s	1570m,b	548s	440vs, 385s, 360s
$TiCl_4(asp)_2$	3440m, 3325m			1600m	560s	390s
$ZrCl_4(asp)_2$	3430m, 3322m			1612m	570w	348m
ap		1582sh,	1505w	1665vs		
$SnCl_4(ap)_2$*					460w	330s
$SnBr_4(ap)_2$		1598w,	1510w	1550s,b	440m	235s
$SnI_4(ap)_2$		1598m,	1515w	1555vs	440m	**
$GeCl_4(ap)_2$		1592w,	1518w	1562vs	518w	340vs
$ZrCl_4(ap)_2$				1555vs	538m	348s

s = strong, m= medium, w= weak, vs = very strong, b = broad

* Ref (122), ** ν(Sn-I) <200 cm^{-1}.

observed in the 1500-1615 cm^{-1} region.

In case of 4-aminoantipyrine three modes of coordination must be considered, unidentate behaviour with bonding through either the oxygen or the amino-nitrogen or chelation utilizing both of these atoms. In all the complexes of 4-aminoantipyrine a negative shift in ν(C=O) after complexation is indicative of coordination through carbonyl oxygen.

The 1:1 complexes of 4-aminoantipyrine shows a marked negative shift in ν(N-H) which may either be due to hydrogen bonding of amino-hydrogen with halogen of metal halide or due to coordination through nitrogen of amino group (132).

Far IR spectra and structure of complexes

Addition compounds of the type $MX_4.L_2$ (where M = Sn, Ge, Ti, Zr, and Si; X = halogen; L = monodentate ligand) are well known although their stereochemistry has only recently been extensively studied. Information of the stereochemistry of coordination compounds of non-transition elements where the lack of partially filled d-shell renders other techniques inapplicable, may be obtained by studying absorption spectra in the far IR region.

If we assume the presence of discrete six-coordinate species, it is necessary to decide between the cis-and trans-configurations. The trans adduct is considered to be similar to a perturbed square

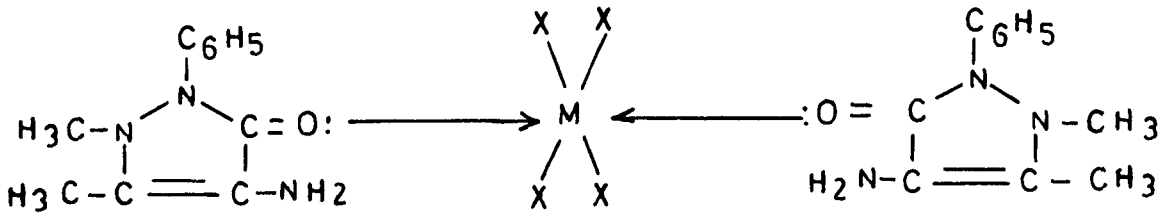
planar MX_4 unit, so that only one infrared active fundamental MX stretching vibration of symmetry type e_u is predicted (97). For the cis-configuration there would be at least two fundamentals associated with MX stretching modes. Beattie and coworkers (105) performed a normal coordinate analysis of the octahedral species cis-and trans-$MX_4.L_2$. For a cis adduct three high frequency bands are to be expected, the next nearest band lying considerably below this group. In the trans adducts if the metal ligand force constant is low compared with that of metal halogen, there will be one main band in the same region as the set of three absorptions mentioned for the cis adduct. However, where the metal ligand force constant is high, the e_u and a_{2u} vibrations will occur in similar regions of the spectrum. Thus in a crystalline compound, crystal field resolution of the e_u vibration to a doublet, plus the presence of an a_{2u} vibration could lead to spectrum similar to that of a cis adduct with the difference that in such a trans compound there is one strong band with the remaining bands being of weaker intensity.

The 1:1 complexes of 4-aminoantipyrine could be formulated as (a) a five-coordinated monomer with monodentate ligand, (b) a cis-octahedral monomer with bidentate ligand, (c) a chain polymer with octahedrally coordinated metal atom bridged by ligand molecules arranged cis or trans to each other, or (d) an octahedral structure with monodentate ligand involving halogen bridges.

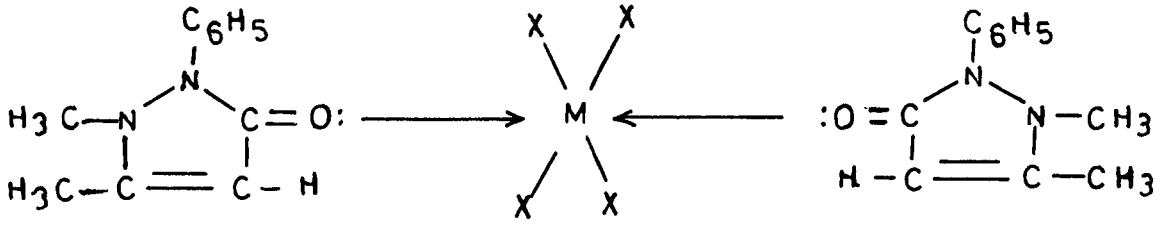
The structures are determined primarily by the ligand rather than by halogen. Those ligands having a polarizable π-bond linkage behind the spear head atom give cis-complexes with tin halides (11, 133). Thus overlap of π-bonding charge cloud of the ligand with an empty d-orbital of the central atom plays a significant part in the linkage and the stronger bonding of ligands develops through the use of two different d-orbitals required for the cis-complex.

The low frequency IR spectra of the complexes have been recorded with a view to distinguishing between the terminal ν(M-X) and the bridging ν(M-X-M) stretching vibrations and also to locate the metal-ligand vibrations. The bands which are virtually unaffected by changing halogen are attributed to the ν(M-O) modes. In the spectrum of the complexes irrespective of the Lewis acid taken new bands are observed in the 440-570 cm^{-1} region which can be assigned to ν(M-O).

The ν(M-X) usually appears as a strong band and shifts to lower frequency with the increase in size of halogen. The ν(Sn-I) could not be observed in the spectral range studied. In 1:2 (MX_4: ligand) complexes the presence of only one ν(M-X) band is indicative of a trans-octahedral geometry (point group D_{4h}) (105) (Fig. III). However, in $GeCl_4(asp)_2$ the appearance of three ν(M-Cl) bands is attributable to a cis-octahedral geometry (Fig. IV).



(M=Ge, Ti, Zr)



(M=Ge, Zr, X=Cl and M=Sn, X=Cl, Br, I)

Fig. III

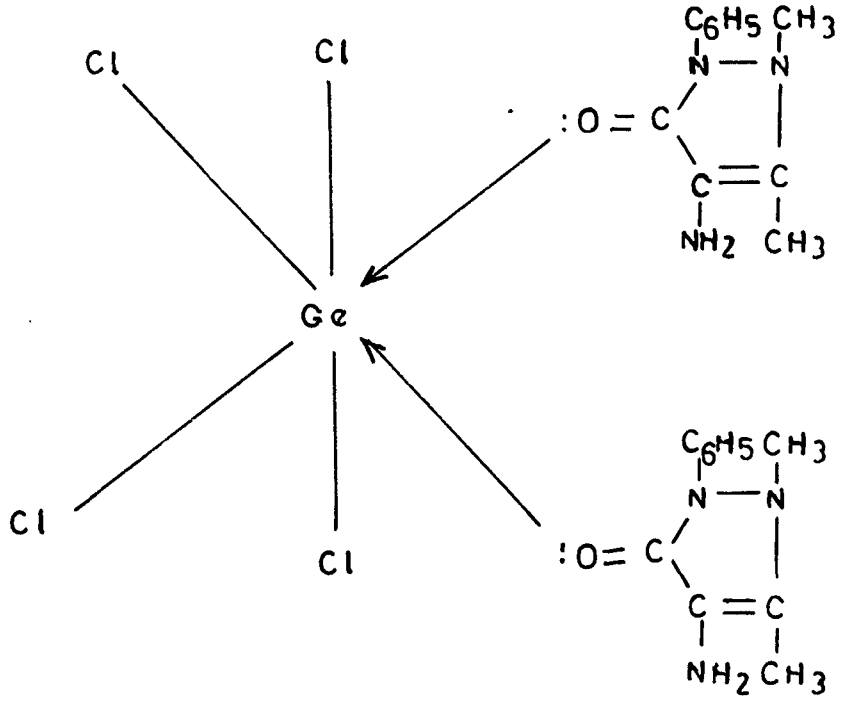


Fig. IV

The tin (IV) chloride and bromide complexes of 4-aminoantipyrine formed in a 1:1 ratio also have only one stretching band at 330 cm^{-1} and 240 cm^{-1}, respectively. Calculations of ν(Sn-Br)/ν(Sn-Cl) ratio for a large number of octahedral complexes show that this ratio varies from 0.71 to 0.76 (134, 135). For octahedral 1:2 complexes of antipyrine this ratio is 0.71, and for 1:1 complexes of 4-aminoantipyrine it is 0.72. The close similarity between the spectra of 1:2 and 1:1 complexes of tin (IV) in ν (Sn-X) region indicates similar environment in both types of complexes, thereby ruling out the possibility of a five-coordinated tin in the case of 1:1 complexes. To account for the stoichiometry required for octahedral structure the sixth coordination site must be satisfied by a bridged halogen or a ligand molecule. A bridging (M-X-M) stretching vibration would be expected to be found at a lower frequency (134) in comparison with a terminal ν (M-X) vibration. The shift of a ν (M-X) vibration to lower frequency upon bridging is well understood, since each halogen atom bridges two different metal atoms. In contrast to this, the metal ligand vibration would not be expected to shift significantly upon bridging, since for ligand the bridging is through two different atoms rather than the same atom. As there is no evidence for the halogen bridging, these complexes are, therefore, postulated as trans-octahedral compounds (Fig. V) involving ligand bridging

through the carbonyl oxygen and the amino-nitrogen. The ν(M-N) bands, however, could not be distinguished unambiguously from the ligand internal modes.

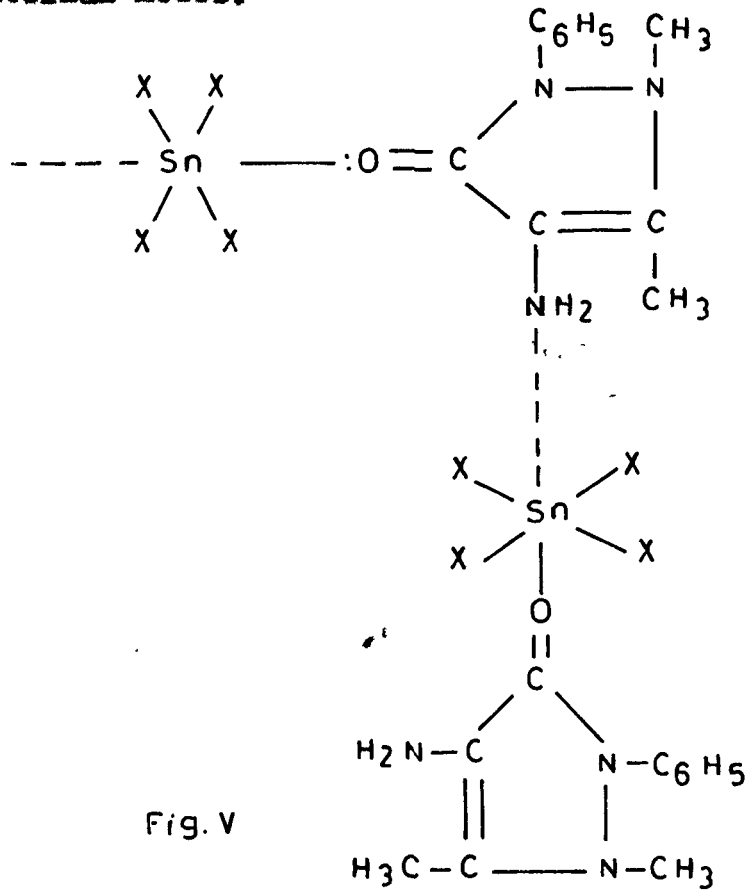


Fig. V

It is, therefore, concluded that 4-aminoantipyrine in 1:1 complexes prefers to act as a chelating bidentate ligand, whereas, in the 1:2 complexes, it acts as a terminal unidentate ligand. It is quite expected that when coordination takes place from one site, the electron demand from another coordination site makes it less basic and a 1:2 type of complex is formed.

CHAPTER - IV

COMPLEXES OF GROUP (IV) METAL HALIDES WITH PIPERAZINE 1,4-DICARBODITHIOATE

COMPLEXES OF GROUP (IV) METAL HALIDES WITH PIPERAZINE 1,4-DICARBODITHIOATE

The transition metal complexes (137-139) of dithiocarbamates (carbodithioate) have extensively been studied. However, there have been limited studies on group (IV) metal complexes (41-43, 140; 141). Pretti et al., (142) have recently reported the transition metal complexes of piperazine 4-carbodithioate and N-methyl piperazine 4-carbodithioate. Eight coordinated titanium (IV) complexes of dithiocarbamates have also been reported (43, 140). Most of the studies on complexing properties of bis-dithiocarbamates or dicarbodithioates are concerned with piperazine derivatives (44, 137, 143) containing two CS_2^- groups at two ends of the heterocyclic ring which form polymeric chelates insoluble in water and numerous organic solvents. It was, therefore, of interest to synthesize and characterise the complexes of tetrahalides of group (IV) elements with piperazine 1,4-dicarbodithioate (piperazine bis-dithiocarbamate, Pzdtc) and to explore the possibility of formation of polymeric chelated species.

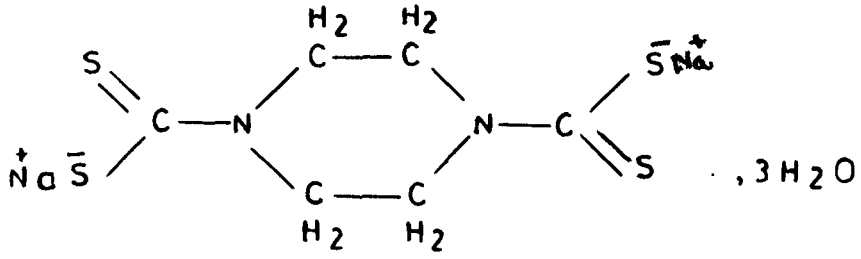
EXPERIMENTAL

Preparation and Standardization of Stock Solution of Silicon Tetrachloride:

Anhydrous silicon tetrachloride was standardised by hydrolysing it with ammonia solution and weighing the dried precipitate as SiO_2 from this weight of SiO_2 the amount of $SiCl_4$ was calculated in the solution.

Preparation of the Ligand:

Sodium piperazine 1,4-dicarbodithioate $[Na_2(Pzdtc).3H_2O]$ (Fig. VI) was prepared by treating piperazine with carbon



disulphide and sodium hydroxide. An aqueous solution of sodium hydroxide was added under vigorous stirring for about four hours to carbon disulphide and piperazine hexahydrate dissolved in isopropyl alcohol and dry ethyl ether mixture. The reactants were taken in the molar ratios: amine: carbon disulphide: sodium hydroxide = 1:2:2.

Preparation of the Complexes:

Dichloro (piperazine 1,4-dicarbodithioato) tin (IV) [$SnCl_2$ (Pzdtc)]: Both sodium piperazine 1,4-dicarbodithioate and tin (IV) chloride were taken in alcohol in equimolar ratio. On addition of the ligand solution to the metal chloride solution a yellow coloured complex appeared which was washed with alcohol and dried in vacuum over calcium chloride.

Dibromo (piperazine 1,4-dicarbodithioato) tin (IV) [$SnBr_2$ (Pzdtc)]: This complex was prepared by the same procedure as described for the chloro compound, i.e., by the addition of an alcoholic solution of the ligand to the metal halide solution in stoichiometric amount. A yellow coloured complex appeared after stirring the mixture for a few minutes which was washed with alcohol and dried in vacuum.

Diiodo (piperazine 1,4-dicarbodithioato) tin (IV) [SnI_2(Pzdtc)]: A chloroform solution of the ligand was added to the metal halide solution also in chloroform in equimolar ratio which gave a thick-yellow coloured complex which was purified and dried in usual manner.

Dichloro bis-(hydrogen piperazine 1,4-dicarbodithioato) germanium (IV) [$GeCl_2H_2(Pzdtc)_2$]: The metal halide and ligand were taken in chloroform in a 1:2 ratio. The addition of metal chloride solution to the ligand solution gave a crystalline

white coloured substance. It was purified with chloroform and dried in vacuum over calcium chloride.

Dichloro bis-(hydrogen piperazine 1,4-dicarbodithioato) silicon (IV) $[SiCl_2H_2(Pzdto)_2]$: Anhydrous silicon (IV) chloride in chloroform was added slowly to the solution of the ligand in chloroform. A white coloured microcrystalline precipitate appeared which was dried in vacuum after purification.

Dichloro bis-(hydrogen piperazine 1,4-dicarbodithioato) titanium (IV) $[TiCl_2H_2(Pzdto)_2]$: Stoichiometric amount of titanium (IV) chloride was added to the ligand solution in absolute alcohol. A yellow coloured precipitate appeared which was washed and dried in vacuum.

Hexachloro (piperazine 1,4-dicarbodithioato) zirconium (IV) $[Zr_2Cl_6(Pzdto)]$: Zirconium (IV) chloride was shaken in an excess of alcohol to dissolve the maximum amount of $ZrCl_4$. The ligand was also taken in the same solvent. On mixing the two solutions a black coloured precipitate appeared which was washed with alcohol and dried in vacuum.

<u>Reactions Involved in the Formation of Complexes</u>:

$$SnX_4 + C_6H_8N_2S_4Na_2.3H_2O \rightleftharpoons SnX_2C_6H_8N_2S_4 + 2NaX + 3H_2O$$

[X = Cl, Br, I]

$$2ZrCl_4 + C_6H_8N_2S_4Na_2.3H_2O \rightleftharpoons Zr_2Cl_6C_6H_8N_2S_4 + 2NaCl + 3H_2O$$

$$MCl_4 + 2C_6H_8N_2S_4Na_2.3H_2O \rightleftharpoons MCl_2(C_6H_8N_2S_4H)_2 + 2NaCl + 2NaOH + 4H_2O$$

[M = Ge, Si, Ti]

RESULTS AND DISCUSSION

All the complexes are stable at room temperature. The analytical data along with colour and melting points of the complexes have been presented in Table 5. The complexes formed have the composition $SnX_2(Psdtc)$ (X = Cl, Br and I), $MCl_2H_2(Psdtc)_2$ (M = Ge, Si and Ti) and $Zr_2Cl_6(Psdtc)$. The complexes are insoluble in usual organic solvents. However, tin (IV) halide complexes are just sufficiently soluble in dimethylformamide (10^{-3}M) to enable their molar conductivity measurements. The comparison of the molar conductance values with those of typical uni-univalent electrolytes in dimethylformamide (10^{-3}M) indicate that these complexes are basically non ionic in nature. It falls in the range 50-55 $ohm^{-1}cm^2mole^{-1}$ indicating their non ionic nature (114).

Some important IR bands of the free ligand and its complexes are recorded in Table 4. The ν(OH) bands at 3400 and 3270 cm^{-1}, and δ(HOH) bands at 1610 and 1590 cm^{-1} in the ligand spectrum indicate the presence of lattice water (144).

The ν(C---N) bands observed at 1455 cm^{-1} in the ligand is at a lower frequency in comparison to ν(C---N) of diethyldithiocarbamate (1477 cm^{-1}) (145). This difference is also reflected in these complexes. Those of diethyldithiocarbamate being at a higher frequency than those of Psdtc. Piperazine

TABLE - 3

Colour, melting point and analytical data of the complexes

Complex	Colour	M.P. (°C)	% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% S Found (Calcd)	% M Found (Calcd)	% X Found (Calcd)
$Na_2(Psdtc).3H_2O$	White	300D	20.48 (21.42)	4.81 (4.16)	8.16 (8.33)	37.20 (38.09)		
$SnCl_2(Psdtc)$	Yellow	275	16.12 (16.99)	2.10 (1.90)	6.63 (6.56)	29.18 (30.07)	25.49 (27.83)	15.89 (16.60)
$SnBr_2(Psdtc)$	Yellow	285	13.17 (14.06)	1.22 (1.56)	4.98 (5.43)	24.65 (24.88)	25.01 (22.98)	30.48 (31.01)
$SnI_2(Psdtc)$	Yellow	290	11.78 (11.91)	1.41 (1.32)	5.22 (4.59)	20.39 (21.04)	20.13 (19.48)	40.96) (41.65)
$GeCl_2H_2(Psdtc)_2$	White	326D	22.88 (23.41)	2.28 (2.93)	10.02 (9.04)	40.68 (41.42)		11.36 (11.45)
$SiCl_2H_2(Psdtc)_2$	White	280D	24.84 (25.22)	2.79 (3.15)	10.12 (9.74)	43.94 (44.63)		11.98 (12.33)
$TiCl_2H_2(Psdtc)_2$	Yellow	285D	25.13 (24.58)	2.87 (3.05)	10.12 (9.42)	42.87 (43.15)	7.66 (9.05)	10.98 (11.92)
$Zn_2Cl_6(Psdtc)$	Black	300D	12.12 (11.46)	1.25 (1.27)	4.08 (4.43)	19.89 (20.29)	27.68 (28.87)	32.98 (33.65)

D = decomposition temperature

TABLE - 4

IR spectra of the ligand and complexes

Compound	ν (C—N)	ν (C—S)	ν (M—Cl)
Na_2(Pzdtc).$3H_2O$	1455vs,b	1000vvs	
$SnCl_2$(Pzdtc)	1455vs,b	1000s	395s
$SnBr_2$(Pzdtc)	1460vs,b	1015m	320s
SnI_2(Pzdtc)	1460vs	1000s	370w
$CeCl_2H_2$(Pzdtc)$_2$	1452vvs	1000vs,965m	418m
$SiCl_2H_2$(Pzdtc)$_2$	1450vs	1030sh,940vs	*
$TiCl_2H_2$(Pzdtc)$_2$	1452vvs	998s ,962s	372w
Zr_2Cl_6(Pzdtc)	1455vs,b	1000vs	368w

* ν (M—S) obscured by intense and broad 455 cm^{-1} ν (Si—Cl) mode

shows less tendency to release electrons to the carbon and nitrogen bond due to its rigid ring system and as a consequence the carbon-nitrogen bond has less double bond character.

The dithiocarbamato group may act as an unidentate (146) or bidentate (137) donor forming a four-membered chelate ring. A doublet is expected in the region 1000 ± 70 cm^{-1} in the unchelated dithiocarbamate (141). In the tin (IV) and zirconium (IV) complexes the presence of only one ν (C—S) band indicates chelation of the dithiocarbamato moiety. However, in Ge(IV), Si(IV) and Ti(IV) complexes there is a splitting of this band which may either be due to the unidentate behaviour of ligand or due to the presence of both coordinated and uncoordinated dithiocarbamato groups.

The ν (S—H) vibration occur usually in the range 2600-2550 cm^{-1} (66). However, Sweeney et al., (68) have observed this band at 2550 cm^{-1} in the liquid 1,2-dimercaptoethane. Dithioacetic acid absorbs at 2481 cm^{-1} (66). In the Ge(IV), Si(IV) and Ti(IV) complexes, there is appearance of weak or medium intensity bands in 2530-2450 cm^{-1} region which are absent in other complexes and ligand spectra. These bands are attributable to ν (S—H) absorption. Their shift to lower spectral region seems to be due to hydrogen bonding (66). The appearance of ν (S—H) vibration bands in these complexes indicate that a proton is attached to each uncoordinated

dithiocarbamato group.

The far IR region (650-200 cm^{-1}) is very important for structure elucidation since this region contains the metal-halogen and metal-ligand vibrations which could possibly give an insight into the nature of the bridging occuring in these complexes. There are four peaks in the region 650-200 cm^{-1} at 498, 415, 350, 332 cm^{-1} in the ligand spectrum. In these complexes new peaks appear in the 368-408 cm^{-1} region which are attributable to ν(M-S) (41, 43, 140).

The ν (M-Cl) vibrations which are inherently strong are useful in deducing the stereochemistry of the complexes. Generally, $SnCl_4$ forms hexacoordinated complexes of the type $SnCl_2$(dithiocarbamates)$_2$ (41, 42, 141) involving bidentate dithiocarbamates, so that a hexacoordinated structure is also likely for SnY_2(Psdtc) complexes involving ligand bridging through the dithiocarbamato group. For the octahedral cis-isomer, both symmetric and asymmetric ν (Sn-X) modes are infrared active (147). In $SnCl_2$(Psdtc) the presence of only one ν (Sn-Cl) band at 295 cm^{-1} indicates that the chlorine atoms occupy a trans position in the octahedron (Fig. VII). In the Ge(IV), Si(IV) and Ti(IV) complexes there is only one strong ν (M-Cl) stretching band at 340, 455 and 350 cm^{-1}, respectively, which is indicative of a trans stereochemistry (Fig. VIII).

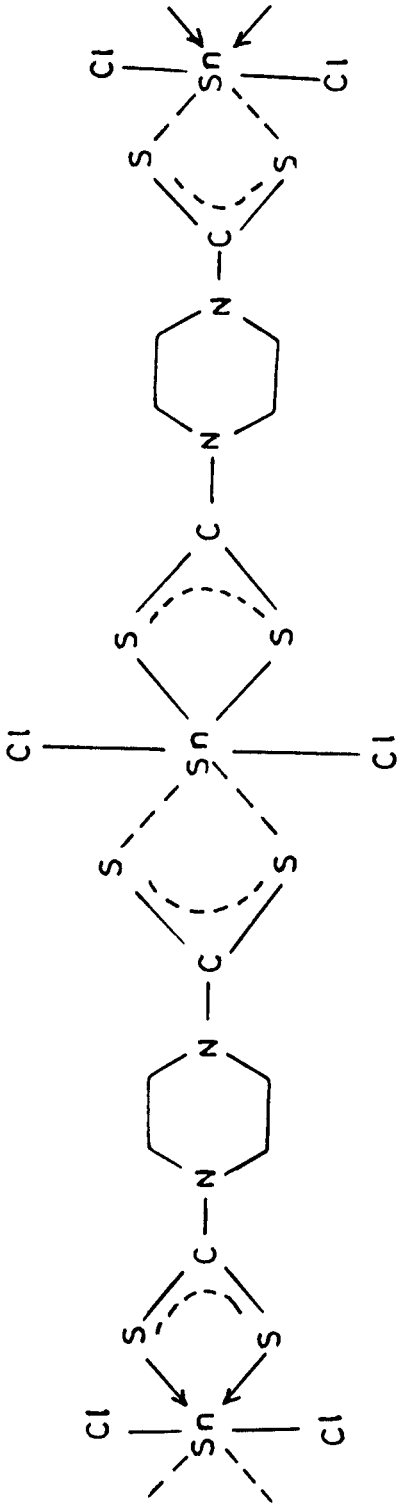
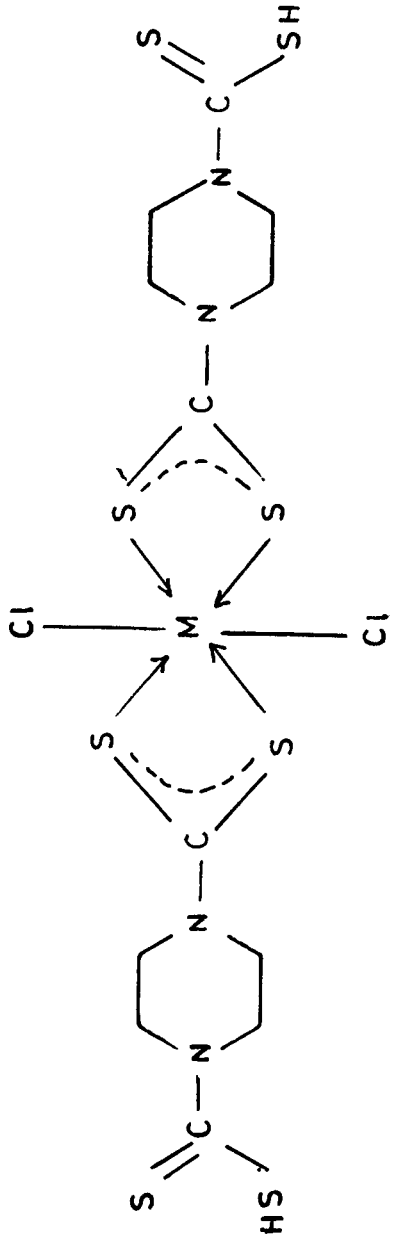


Fig. VII



(M = Ge, Si, Ti)

Fig. VIII

CHAPTER - V

COMPLEXES OF GROUP (IV) METAL HALIDES WITH BENZO (f) QUINOLINE

COMPLEXES OF GROUP (IV) METAL HALIDES WITH BENZO (f) QUINOLINE

During recent years several studies on the metal complexes of quinolines have been reported (54, 55, 148-150). Benzo quinolines are of much interest owing to their biological importance. Most of the studies of benzo quinoline complexes are with transition metals. Benzo (f) quinoline (5,6-benzo quinoline) (Fig. IX) has been reported to form a complex with chromium tricarbonyl (54). There is no report on the complexes of benzo (f) quinoline with halides of group (IV) elements. Complexes of benzo (f) quinoline (bfq) with group (IV) metal halides, viz. $SnCl_4$, $SnBr_4$, SnI_4, $CeCl_4$, $SiCl_4$, $TiCl_4$ and $ZrCl_4$, have presently been synthesized and characterized.

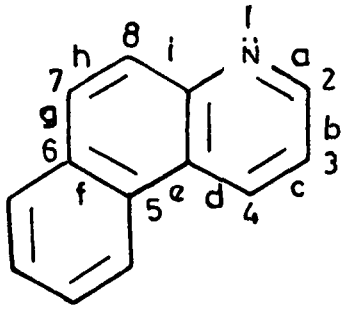


FIG. IX

EXPERIMENTAL

Benzo (f) quinoline (m.p. 160°C) (E. Merk) was used as such.

Preparation of the Complexes:

Tetrachloro [benzo (f) quinoline] tin (IV) [$SnCl_4(bfq)$]: An alcoholic solution of tin (IV) chloride was mixed with an alcoholic solution of ligand in 1:1 metal to ligand ratio. A yellow solid compound was precipitated immediately, which was filtered and washed several times with the solvent. It was dried over calcium chloride in vacuum.

Tetrabromo [benzo (f) quinoline] tin (IV) [$SnBr_4(bfq)$]: An alcoholic solution of the ligand was added to an alcoholic solution of tin (IV) bromide in equimolar ratio. After standing the mixture for half an hour a pale yellow coloured complex appeared which was washed with alcohol and dried in vacuum over calcium chloride.

Tetraiodo bis-[benzo (f) quinoline] tin (IV) [$SnI_4(bfq)_2$]: On mixing chloroform solution of tin (IV) iodide and the ligand in equimolar ratio a dark yellow coloured precipitate appeared which was purified and dried in the usual manner.

Tetrachloro [benzo (f) quinoline] germanium (IV) [$GeCl_4(bfq)$]: A chloroform solution of germanium (IV) chloride was mixed with the ligand solution in the same solvent. A pale yellow coloured

complex appeared, which was washed with chloroform and dried in vacuo.

Tetrachloro bis-[benzo (f) quinoline] silicon (IV) $[SiCl_4(bfq)_2]$: Chloroform solution of silicon (IV) chloride was mixed with chloroform solution of the ligand in equimolar ratio. A pale yellow complex appeared which was washed with the solvent and dried in vacuum over calcium chloride.

Tetrachloro bis-[benzo (f) quinoline] titanium (IV) $[TiCl_4(bfq)_2]$: An alcoholic solution of metal halide was added to an alcoholic solution of the ligand in equimolar ratio. Whereupon a white complex separated from the reaction mixture.

Tetrachloro [benzo (f) quinoline] zirconium (IV) $[ZrCl_4(bfq)]$: Zirconium (IV) chloride was dissolved in an excess of alcohol. To this solution the ligand solution was added in equimolar ratio. A white complex was formed which was washed with the solvent and dried in vacuo.

RESULTS AND DISCUSSION

The analytical data along with the colour and melting point of the complexes have been presented in Table 5. Comparison of molar conductance values (Table 5) of 10^{-3}M solution in dimethylformamide with those of typical uni-univalent electrolytes in this solvent indicate that these complexes are basically non-ionic in nature (114). Zirconium (IV) chloride complex is insoluble in usual organic solvents. The molar conductance of silicon (IV) chloride complex, which is insoluble in dimethylformamide, has been measured in nitrobenzene.

The assignments of the various IR bands of benzo (f) quinoline and its complexes in the 4000-200 cm^{-1} have been presented in Table 6. Characteristic aromatic ring vibrations appear in the range 1600-1350 cm^{-1} in most of the heterocyclic compounds (57). The ring stretching vibrations probably result from the complete interaction of ν(C=C) and ν(C=N) vibrations, and it is, therefore, very difficult to distinctly identify these vibrations. Coordination through the ring nitrogen atom causes an increase in the C=C and C=N stretching frequencies (151, 152) in donor molecules similar to benzo (f) quinoline, viz., pyridine, quinoline and pyrimidine (136,151,152). In benzo (f) quinoline complexes the ring stretching vibrations appear in the higher frequency region (1640-1452 cm^{-1}) as

TABLE - 5

Colour, melting point, analytical data and molar conductance* of the benzo (f) quinoline complexes

Complex	Colour	M.P °C	% C Found (calcd)	% H Found (calcd)	% N Found (calcd)	% X Found (Calcd)	% M Found (calcd)	Λ_m ohm^{-1} cm^2 mole^{-1}
$SnCl_4(bfq)$	Yellow	230	34.60 (35.50)	1.98 (2.06)	3.49 (3.18)	32.05 (32.23)	25.6 (26.98)	54.2
$SnBr_4(bfq)$	Yellow	220	24.80 (25.27)	1.30 (1.47)	1.92 (2.27)	50.02 (51.75)	18.50 (19.21)	49.1
$SnI_4(bfq)_2$	Brownish-Yellow	180	30.20 (31.71)	1.98 (1.84)	3.10 (2.84)	49.99 (51.54)	11.80 (12.05)	45.8
$GeCl_4(bfq)$	Yellow	220	38.12 (39.63)	1.96 (2.30)	3.27 (3.55)	36.82 (36.00)		48.7
$SiCl_4(bfq)_2$	Yellow	290D	59.54 (59.12)	2.80 (3.43)	4.90 (5.30)	25.51 (26.83)		15.6*
$TiCl_4(bfq)_2$	White	235	57.21 (56.97)	2.90 (3.31)	5.28 (5.11)	24.98 (25.86)	7.65 (8.74)	55.8
$ZrCl_4(bfq)$	White	285D	36.26 (37.84)	2.01 (2.20)	3.08 (3.39)	33.87 (34.39)	22.68 (23.30)	

D = decomposition temperature, *Λ_m of 10^{-3}M solution in dimethylformamide
**Λ_m of 10^{-3}M solution in nitrobengene.

TABLE - 6

Assignments of IR spectra (4000-200 cm^{-1}) of benzo (f) quinoline and its complexes

Assignments	bfq	$SnCl_4$(bfq)	$SnBr_4$(bfq)	SnI_4(bfq)$_2$	$CeCl_4$(bfq)	$SiCl_4$(bfq)$_2$	$TiCl_4$(bfq)$_2$	$ZrCl_4$(bfq)
ν(C=C) and ν(C=N)	1600w 1580w 1560w 1485sh 1445vvs	1610m 1585w 1550w 1505m 1460vvs	1615m 1600w 1555m 1500m 1455vvs	1615s 1590m 1550m 1505s 1452vvs	1630w 1600w 1550m 1500s 1455vvs	1640m 1610w 1565m 1518m 1460vs	1640w 1620m 1560m 1510w 1460vvs	1620w 1565w 1515w 1460vvs
CH in plane def.	998m 975w	1000w 965m	1000w 990w	1010w 980m	990m 960m	1000w 970m	990m 965s	1000w 965w
CH def.	710s	700s	700vs	705s	705vs	710s	705s	710w
ν(M-X)		340s 270s			415vs 335vvs	425s	428s	355m
ν(M-N)		295w		325w	320sh	330m	335w	328w

compared to those of the free ligand at 1600, 1580, 1560, 1485, 1445 cm^{-1}.

The region of 4000-650 cm^{-1} is a poor region to get any conclusive evidence regarding the structure of the complexes, since in this region one is dealing only with ligand vibrations, modified by complexation. The region below 650 cm^{-1} is very important for structure elucidation. This region contains, the metal-halogen and metal-ligand vibrations, and thus, may be quite useful in determining the stereochemistry of the complexes. Observation of the position of the low frequency infrared vibrations could possibly give an insight into the nature of the bridging occurring in these complexes.

It is known that with smaller donor species metals form adducts having the two ligands in the cis position, whereas, with bulky ligands they form trans-octahedral species due to steric reasons (133). A trans-octahedral species should exhibit one infrared active ν(M-X) mode (e_u symmetry). However, the cis-isomer is expected to have four such modes ($2a_1 + b_1 + b_2$) (105).

On complexation new bands appear in the region 295-335 cm^{-1} which are attributable to ν(M-N) modes. The ν(M-Cl) bands are inherently strong and are useful in determining the stereochemistry of the complexes. The complexes formed have

the composition $MX_4(bfq)_2$ or $MX_4(bfq)$. Appearance of only one ν(M-X) band in $MX_4(bfq)_2$ type of complexes indicates a trans-octahedral environment (105) of the metal ion in these complexes (Fig. X)

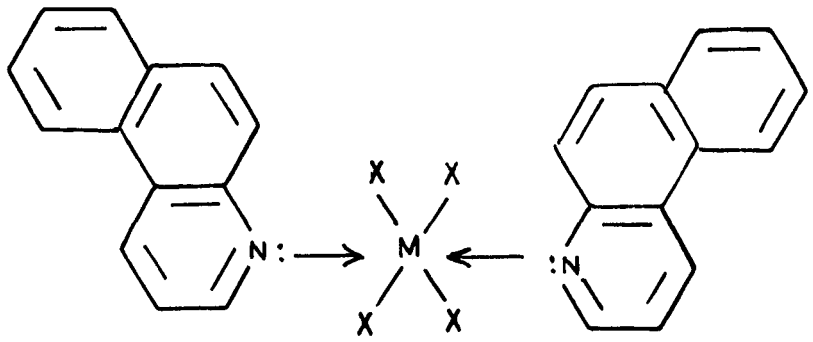


FIG. X

The $MX_4(bfq)$ type complexes could be formulated as a five coordinated monomer or a hexacoordinated polymer involving halogen bridges. In $MX_4(bfq)$ complexes two ν(M-Y) bands may be attributed to terminal and bridged halogen atoms. A bridged halide would be expected to be found at lower frequency (134, 153). The shift of a ν(M-X) vibration to lower frequency

upon bridging is well understood, since each halogen atom bridges two different metal atoms. The ν(M-X) vibration bands in $SnCl_4$ and $GeCl_4$ complexes show a marked shift of 70 and 80 cm^{-1}, respectively, which may be attributable to bridging ν(M-X) vibrations. However, in the IR spectrum of $ZrCl_4$(bfq) the bridging ν(M-X) band could not be detected. The position of terminal ν(M-Cl) vibrations in these complexes is in the region as reported for the hexacoordinated complexes of the type $MX_4.2L$ (27, 136, 153). Thus, the $SnCl_4$(bfq) and $GeCl_4$(bfq) complexes could be formulated as octahedral complexes involving halogen bridges (Fig. XI).

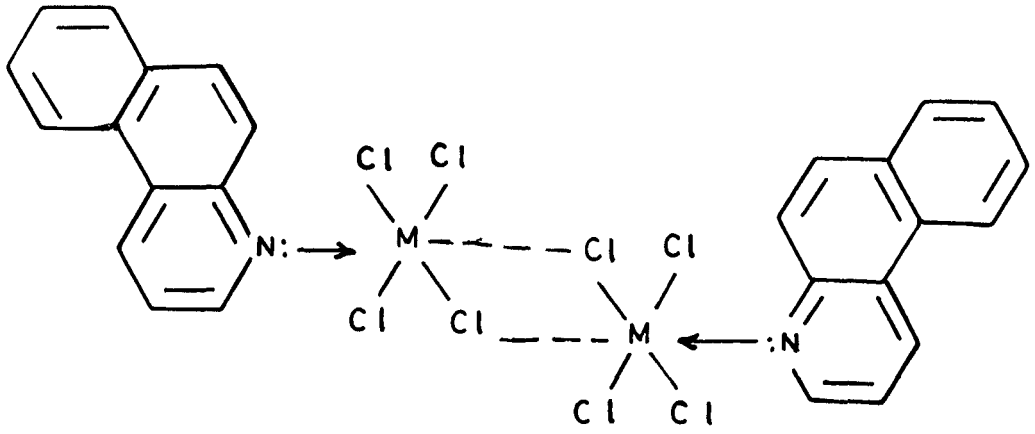


FIG. XI

CHAPTER - VI

COMPLEXES OF GROUP (IV) METAL HALIDES WITH BENZO (c) QUINOLINE

COMPLEXES OF GROUP (IV) METAL HALIDES WITH BENZO (C) QUINOLINE

Benzo (h) quinoline (7,8-benzo quinoline) has been found to act as an electron pair donor through ring nitrogen and simultaneously also forming a metal-carbon σ-bond through the aromatic carbon (53) Benzo (b) quinoline (acridine) complexes of group (IV) metal halides (155-157) have earlier been reported from this laboratory. In the preceding chapter benzo (f) quinoline complexes of group (IV) metal halides have been discussed.

Presently the complexes of another angular, homologue, i.e., benzo (c) quinoline (3,4-Benzoquinoline, phenanthridine) (Fig. XII), have been prepared and characterized with a view to studying its relative coordinating efficiency in comparison to other benzo quinolines. The complexes of benzo (c) quinoline (bcq) with group (IV) metal halides, viz., $SnCl_4$, $SnBr_4$, SnI_4, $GeCl_4$, $SiCl_4$, $TiCl_4$ and $ZrCl_4$, have presently been reported.

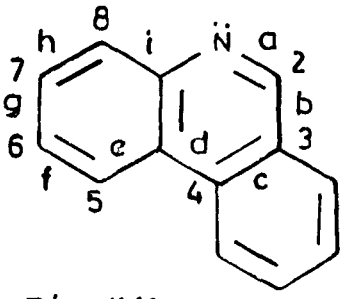


Fig. XII

EXPERIMENTAL

Benzo (c) quinoline (M.P. 110°C) (Fluka A.G.) was used as such.

Preparation of the complexes

Tetrachloro [benzo (c) quinoline] tin (IV) $[SnCl_4(bcq)]$: An alcoholic solution of tin (IV) chloride was mixed with an alcoholic solution of the ligand in an equimolar ratio and heated for about half an hour. A crystalline white complex appeared which was washed with alcohol and dried over calcium chloride in vacuum.

Tetrabromo bis-[benzo (c) quinoline] tin (IV) $[SnBr_4(bcq)_2]$: An alcoholic solution of the metal bromide was mixed with an alcoholic solution of the ligand in stoichiometric amount which gave a precipitate after keeping the mixture for some time. This precipitate was washed and dried in vacuum.

Tetraiodo bis-[benzo (c) quinoline] tin (IV) $[SnI_4(bcq)_2]$: Chloroform solutions of tin (IV) iodide and ligand on mixing in equimolar ratio gave a yellowish-orange complex, which was washed with the solvent and dried in vacuum.

Tetrachloro [benzo (c) quinoline] germanium (IV) $[GeCl_4(bcq)]$: A chloroform solution of germanium (IV) chloride was mixed with

a chloroform solution of the ligand in equimolar ratio. After keeping the reaction mixture for few minutes a white complex was obtained, which was filtered, washed and dried in vacuo.

Tetrachloro bis-[benzo (c) quinoline] silicon (IV) $[SiCl_4(bcq)_2]$: Chloroform solutions of silicon (IV) chloride and the ligand were mixed in an equimolar ratio. After heating for a few minutes a yellow precipitate was formed, which was filtered, washed and dried in vacuo.

Tetrachloro bis-[benzo (c) quinoline] titanium (IV) $[TiCl_4(bcq)_2]$: An alcoholic solution of titanium (IV) chloride was mixed with an alcoholic solution of the ligand in stoichiometric amount and heated for an hour. A white complex appeared which was washed with hot alcohol and dried in vacuo.

Tetrachloro bis-[benzo (c) quinoline] zirconium (IV) $[ZrCl_4(bcq)_2]$: A white complex was obtained on mixing alcoholic solution of zirconium (IV) chloride and the ligand in equimolar ratio.

RESULTS AND DISCUSSION

The analytical data of the complexes, which agree with the proposed stoichiometries, are presented along with other physical properties in Table 7. The complexes formed have the composition $MX_4(boq)_n$ [for n = 1, M = Sn, Ge, X = Cl, and for n = 2, M = Sn, X = Br, I and M = Si, Ti, Zr, X = Cl]. These complexes are fairly stable at room temperature. The molar conductance of 10^{-3} M solution of tin (IV) complexes in dimethylformamide have been measured at room temperature. Comparison of Λ_m values with those of typical uni-univalent electrolytes in this solvent (114) indicate that tin (IV) complexes are basically non-ionic in nature. However, due to insolubility of other complexes in usual organic solvents their molar conductance could not be measured.

These complexes are characterized on the basis of IR studies in the 4000-200 cm^{-1} region. The assignments of various IR bands of benzo (c) quinoline and its complexes are presented in Table 8. The ring stretching vibrations, which result from complete interaction of the C=C and C=N vibrations, after complexation show a positive shift, however, in some complexes these vibrations remain almost unchanged.

Observation of the position of low frequency infrared vibrations could possibly give an insight to the nature of the binding of the metal to the ligand. The most suitable assignments

TABLE - 7

Colour, melting point, analytical data and molar conductance* of the benzo (c) quinoline complexes

Complex	Colour	M.P °C	% C Found (calcd)	% H Found (calcd)	% N Found (calcd)	% X Found (calcd)	% M Found (calcd)	Λ_m ohm^{-1} cm^2 mole^{-1}
$SnCl_4(bcq)$	White	270D	35.10 (35.50)	2.39 (2.06)	3.26 (3.18)	33.01 (32.23)	25.68 (26.98)	51.50
$SnBr_4(bcq)_2$	Yellow	290D	38.98 (39.19)	2.49 (2.27)	3.74 (3.51)	39.81 (40.12)	13.59 (14.89)	40.60
$SnI_4(bcq)_2$	Yellowish-orange	170D	31.82 (31.71)	1.32 (1.84)	3.19 (2.84)	50.88 (51.54)	11.60 (12.05)	39.60
$GeCl_4(bcq)$	White	280	38.81 (39.66)	1.90 (2.30)	3.27 (3.55)	35.41 (36.00)		
$SiCl_4(bcq)_2$	Yellow	320	58.88 (59.12)	2.93 (3.43)	6.10 (5.30)	25.81 (26.83)		
$TiCl_4(bcq)_2$	White	150D	57.01 (56.97)	3.81 (3.31)	5.81 (5.11)	24.98 (25.86)	8.70 (8.74)	
$ZrCl_4(bcq)_2$	White	350	51.89 (52.79)	3.88 (3.07)	4.16 (4.74)	23.01 (23.96)	14.60 (15.4)	

D = decomposition temperature, *Λ_m of 10^{-3}M solution in dimethylformamide

TABLE - 8

Assignments of IR spectra (4000-200 cm^{-1}) of benzo (c) quinoline and its complexes

Assignments	bcq	$SnCl_4(bcq)$	$SnBr_4(bcq)_2$	$SnI_4(bcq)_2$	$GeCl_4(bcq)$	$SiCl_4(bcq)_2$	$TiCl_4(bcq)_2$	$ZrCl_4(bcq)_2$
ν(C=C) and ν(C=N)	1615s 1585m 1570s 1540w 1520m	1630w 1610w 1560w 1530w	1620w 1600w 1575w	1620w 1610w 1590w 1530w	1610m 1585w 1570w	1626sh 1610m 1595m 1545w 1520w	1626sh 1610m 1595m 1570w 1545w	1615sh 1600sh 1575w 1540w
CH in plane def.	970s	950w	970m,b	960s	965s	960m,b	970m	965w
CH def.	720vs	730m	710m	710s	718s	715s	715m	710s
ν(M-X)		340s 260m			420s 325s	485vs,b	375m	348m
ν(M-N)		320w	308w	310w	335sh	345w	332w,b	322w

are made for metal-halide and metal-ligand vibrations. Irrespective of the Lewis acid taken new bands are found in the region 308-345 cm^{-1}, which may be attributed to ν(M-N) vibrations. The ν (M-X) vibrations shift to lower spectral region with increase in the masses of the halogen and the metal involved. Thus ν (Sn-Br) and ν(Sn-I) vibrations fall in the region below 200 cm^{-1}.

The ν (M-Cl) vibrations in the $SiCl_4(bcq)_2$, $TiCl_4(bcq)_2$ and $ZrCl_4(bcq)_2$ appear at 445, 375 and 348 cm^{-1}, respectively. Existence of only one ν (M-Cl) band in these complexes suggests a trans-octahedral geometry (Fig. XIII) for these complexes.

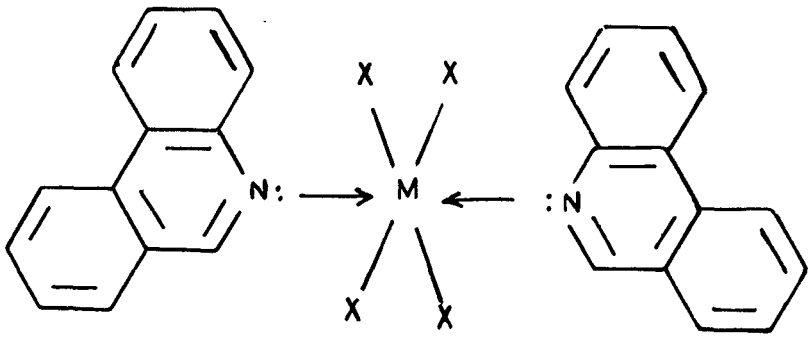


Fig.XIII

A five coordinated trigonal bipyramidal or a hexacoordinated octahedral structure involving halogen bridges can be assigned to the $MX_4(bcq)$ type of complexes. In IR spectra of $SnCl_4(bcq)$ and $GeCl_4(bcq)$ both terminal and bridging ν (M-X) vibrations are

detectable. In the $SnCl_4$(boq) and $GeCl_4$(boq) complexes two ν(M-Cl) vibrations are observed at 340, 260 cm^{-1} and 420, 325 cm^{-1}, respectively. Thus, the ν (M-Cl) vibrations in $SnCl_4$ and $GeCl_4$ complexes are shifted to lower spectral region by 80 and 95 cm^{-1} respectively. This marked shift in ν(M-Cl) vibrations seems due to halogen bridging (134, 153). The position of terminal ν (M-Cl) vibration bands in these complexes is as reported for various hexacoordinated $MCl_4.2L$ type of complexes (27, 136, 154). Thus, an octahedral structure (Fig. XIV) involving halogen bridges is likely for these complexes.

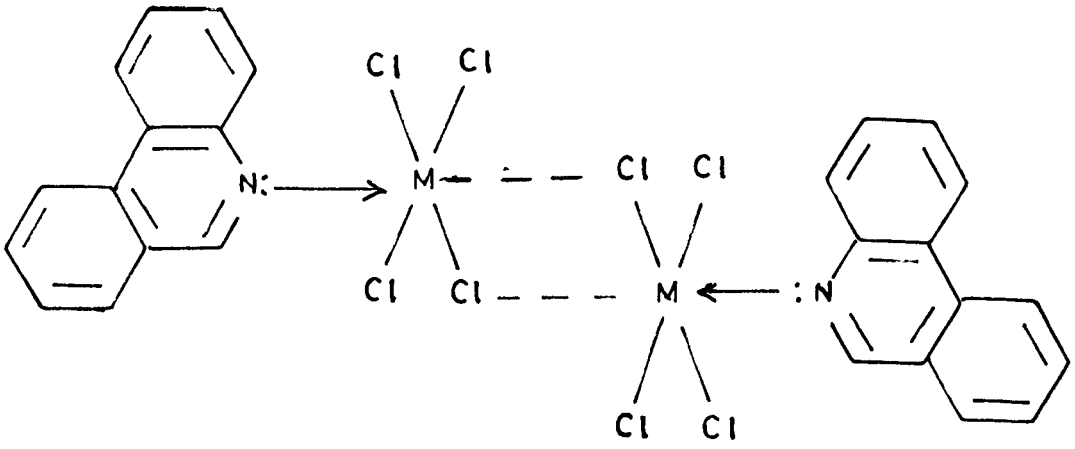


Fig. XIV

CHAPTER - VII

COMPLEXES OF GROUP (IV) METAL FLUORIDES WITH PIPERAZINE 1,4-DICARBODITHIOATE, BENZO (f) QUINOLINE AND BENZO (o) QUINOLINE

COMPLEXES OF GROUP (IV) METAL FLUORIDES WITH PIPERAZINE 1,4-DICARBODITHIOATE, BENZO (f) QUINOLINE AND BENZO (c) QUINOLINE

The tetrafluorides of Group (IV) elements are of two different types: (i) the unassociated and highly volatile compounds (SiF_4 and GeF_4) and (ii) the highly associated and relatively non-volatile solids (SnF_4, TiF_4 and ZrF_4). This differentiation in physical properties is a reflection of the greater tendency of the heavier elements to achieve a maximum degree of coordination i.e., up to six.

While recent studies have shown that tetrafluorides of group (IV) elements coordinate with a variety of ligands (30, 31, 147, 158, 159), information on their coordination behaviour towards simple donor molecules is less extensive than for the remaining group (IV) halides. Generally, the formation of group (IV) tetrafluoride complexes is in the ratio of two molecules of base to one molecule of the fluoride (30, 31, 158) unless, of course, the base is a di- or poly-functional one. A trans-octahedral geometry (31) has been reported for tin (IV) fluoride adducts of pyridine and tetrahydrofuran. Some complexes of group (IV) metal fluorides of the type $MX_4.2L$ (L = amines, triphenyl phosphine oxide and pyridine N-oxide) have been reported to have a cis-octahedral configuration around the metal atom (30, 31). A cis-configuration has been reported for 1:1 adducts where the ligand is

bidentate (31). Infrared spectra of the pyridine N-oxide and triphenyl phosphine oxide derivatives indicate that the ligand-tin bonds are stronger in fluoride than in the chloride complexes.

Muetterties (30) postulated a polymeric octahedral structure involving fluorine bonding for 1:1 adducts of group (IV) metal tetrafluorides with amines. This tendency to form 1:1 polymeric complexes is favoured by the large steric requirements of tertiary amines and is enhanced if the metal fluoride is itself an associated compound. Infrared and NMR studies on difluorobis (acetylacetonato) tin (IV) complex (147) suggest that fluorine atoms occupy a cis-position in the octahedron in the solid state as well as in solution.

There is no report on complex formation of fluorides of tin (IV), titanium (IV) and zirconium (IV) with piperazine bis-dithiocarbamate (Pzdtc), benzo (f) quinoline (bfq) and benzo (c) quinoline (bcq) therefore, an effort was made to synthesize and characterize these complexes.

EXPERIMENTAL

Tin (IV) fluoride (E. Merck), zirconium (IV) fluoride (Koch-Light) and titanium (IV) fluoride (BDH) were used as such without further purification.

Preparation of the complexes

Difluoro (piperazine 1,4-dicarbodithioato) tin (IV) $[SnF_2(Pzdtc)]$: Both sodium piperazine 1,4-dicarbodithioate and tin (IV) fluoride were taken in equimolar ratio. Tetrahydrofuran was used as a solvent. Since in cold there is a possibility of coordination of the solvent itself, tetrahydrofuran was used at its boiling temperature. The tin (IV) fluoride solution was mixed with the ligand solution and refluxed for an hour. The brown coloured solid complex thus formed was extracted from the boiling tetrahydrofuran and was dried in vacuum over calcium chloride.

$$SnF_4 + C_6H_8N_2S_4Na_2.3H_2O = SnF_2C_6H_8N_2S_4 + 2NaF + 3H_2O$$

Difluoro bis-(hydrogen piperazine 1,4-dicarbodithioato) titanium (IV) $[TiF_2(HPzdtc)_2]$: Titanium (IV) fluoride was dissolved in boiling tetrahydrofuran and was mixed with the ligand solution in same solvent in stoichiometric amount. After mixing a white precipitate was formed, which was washed with hot tetrahydrofuran, filtered and dried in vacuo.

$$TiF_4 + 2C_6H_8N_2S_4Na_2.3H_2O = TiF_2(C_6H_8N_2S_4H)_2 + 2NaF + 2NaOH + 4H_2O$$

Difluoro bis-(hydrogen piperazine 1,4-dicarbodithioato) zirconium (IV) $[ZrF_2(HPzdtc)_2]$: A white complex was isolated by treating zirconium (IV) fluoride with the ligand taken in equimolar ratio in boiling tetrahydrofuran.

$$ZrF_4 + 2C_6H_8N_2S_4Na_2.3H_2O = ZrF_2(C_6H_8N_2S_4H)_2 + 2NaF + 2NaOH + 4H_2O$$

Tetrafluoro bis-[benzo (f) quinoline] tin (IV) $[SnF_4(bfq)_2]$: Tin (IV) fluoride and benzo (f) quinoline were taken in equimolar ratio in boiling tetrahydrofuran, which on mixing gave a white coloured complex. It was washed several times with the solvent and dried in vacuum over calcium chloride.

Tetrafluoro bis-[benzo (f) quinoline] titanium (IV) $[TiF_4(bfq)_2]$: Titanium (IV) fluoride was dissolved in hot tetrahydrofuran. The ligand was also taken in the same solvent. Metal and ligand solutions were taken in equimolar ratio and heated for half an hour. After keeping the reaction mixture for an hour a coloured solid compound appeared which was washed with the solvent and dried in vacuo.

Tetrafluoro [benzo (f) quinoline] zirconium (IV) $[ZrF_4(bfq)]$: Solutions of zirconium (IV) fluoride and the ligand were prepared in tetrahydrofuran. The ligand solution was mixed with metal solution slowly in equimolar ratio. The solid product was extracted from the reaction mixture and was dried in vacuum.

Tetrafluoro bis-[benzo (c) quinoline] tin (IV) [$SnF_4(boq)_2$]: Tin (IV) fluoride and ligand solutions were prepared in boiling tetrahydrofuran and were mixed in equimolar ratio. A white complex was obtained which was washed with hot tetrahydrofuran and dried in vacuo.

Tetrafluoro bis-[benzo (c) quinoline] titanium (IV) [$TiF_4(boq)_2$]: Titanium (IV) fluoride and ligand solutions were taken in equimolar ratio in hot tetrahydrofuran. A brown complex was formed which was washed with hot tetrahydrofuran and dried in vacuo.

Tetrafluoro [benzo (c) quinoline] zirconium (IV) [$ZrF_4(boq)_2$]: A yellowish white complex was isolated by treating zirconium (IV) fluoride with ligand taken in equimolar ratio in boiling tetrahydrofuran.

RESULTS AND DISCUSSION

All the complexes are stable at room temperature. The analytical data along with colour and melting point of the complexes have been presented in Table 9. The molar conductances of 10^{-3}M dimethylformamide solution of the complexes have been measured at room temperature. Comparison of these values (Table 9) with those of typical uni-univalent electrolytes in dimethylformamide indicate that these complexes are basically non-ionic in nature (114).

Piperazine 1,4-dicarbodithioate complexes

The IR spectra of piperazine 1,4-dicarbodithioate and its complexes has been recorded in Table 10. The dithiocarbamate group acts as an unidentate or a bidentate donor. In an unchelated dithiocarbamate a doublet is expected in 1000 ± 70 cm^{-1} region (141). Presence of only one ν(C⋯S) band at 995 cm^{-1} in the IR spectra of SnF_2(Pzdtc) indicates the chelation of the dithiocarbamate moiety. However, in the titanium (IV) and zirconium (IV) complexes the ν(C⋯S) band is split either due to unidentate behaviour of the ligand or due to the presence of both coordinated and uncoordinated dithiocarbamato groups. As stated earlier the appearance of new bands in the 2330-2430 cm^{-1} region in the Ge (IV), Si (IV) and Ti (IV) chloride complexes of piperazine 1,4-dicarbodithioate is attributable to the ν(S-H) absorptions. Similarly, in titanium (IV) and

TABLE - 9

Colour, melting point, analytical data and molar conductance* of tin (IV) titanium (IV) and zirconium (IV) fluoride complexes

Compound	Colour	M.P °C	% C Found (calcd.)	% H Found (calcd.)	% N Found (calcd.)	% M Found (calcd.)	% S Found (calcd.)	Λ_m ohm^{-1} cm^2 mole^{-1}
SnF_2(Pzdto)	Brown	290	18.75 (18.33)	2.80 (2.05)	6.83 (7.13)	28.32 (30.20)	32.19 (32.63)	50
TiF_2(HPzdto)$_2$	White	190D	24.89 (25.71)	2.81 (3.23)	9.90 (9.99)	8.05 (8.54)	45.01 (45.75)	53
ZrF_2(HPzdto)$_2$	White	210D	23.01 (23.86)	2.12 (3.00)	10.27 (9.27)	14.94 (15.10)	41.81 (42.47)	51
SnF_4(bfq)$_2$	White	190	55.89 (56.46)	2.91 (3.28)	6.01 (5.06)	20.82 (21.46)		44
TiF_4(bfq)$_2$	Yellow	280	63.84 (64.75)	3.22 (3.76)	5.32 (5.81)	8.56 (9.93)		48
ZrF_4(bfq)	Light Yellow	295	44.89 (45.07)	2.01 (2.62)	3.78 (4.04)	25.81 (26.33)		45
SnF_4(beq)$_2$	White	110	55.23 (56.46)	2.84 (3.28)	6.23 (5.06)	20.10 (21.46)		50
TiF_4(beq)$_2$	Brown	250	63.81 (64.75)	2.84 (3.76)	6.42 (5.81)	10.01 (9.93)		52
ZrF_4(beq)	Yello-wish white	>360	44.81 (45.07)	4.97 (2.62)	3.71 (4.04)	25.72 (26.33)		49

D = decomposition temperature, * Λ_m of 10^{-3}M solution in dimethylformamide

TABLE - 10

IR spectra of sodium piperazine 1,4-dicarbodithioate and its complexes

Compound	Assignments			
	ν(C—N)	ν(C—S)	ν(M—X)	ν(M—S)
$Na_2Pzdtc.3H_2O$	1455vs,b	1000vvs		
$SnF_2(Pzdtc)$	1450vvs	995s	545m,b	390w
$TiF_2(HPzdtc)_2$	1455vvs	1015m, 995s	568s	370w
$ZrF_2(HPzdtc)_2$	1450vvs	1002m,b 965m	470m	372w

zirconium (IV) fluoride complexes 2320 and 2330 cm^{-1} bands, respectively, are attributable to ν(S-H) absorptions. The appearance of ν(S-H) vibration bands in these complexes indicate that a proton is attached to each uncoordinated dithiocarbamate group.

The 545 cm^{-1} band in the SnF_2(Pzdtc) complex is assigned to ν(Sn-F). The position of this band is in the region as reported for various octahedral tin (IV) fluoride complexes (31, 147). Thus, a trans-octahedral structure, involving ligand bridging through the dithiocarbamato group, is proposed for the SnF_2(Pzdtc) complex.

In the octahedral complexes of titanium and zirconium tetrafluorides (160) the ν(Ti-F) and ν(Zr-F) bands are reported to occur in the 550-670 and 453-570 cm^{-1} region, respectively. In the titanium (IV) and zirconium (IV) complexes presence of only one ν(M-F) band at 568 and 470 cm^{-1}, respectively indicate a trans-octahedral stereochemistry. Thus, piperazine bis-dithiocarbamate acts as a quadridentate ligand in the tin (IV) fluoride complex and as a bidentate ligand in the titanium (IV) and zirconium (IV) complexes. On complexation new bands appear in the 370-390 cm^{-1} region which are attributable to ν(M-S) modes.

Benzo (f) quinoline and benzo (c) quinoline complexes

The assignments of the various IR bands of bfq, and bcq and

their complexes have been presented in Table 11. After complexation the ring stretching vibrations (C=C and C=N stretching) show a positive shift, however, in tin (IV) complexes these vibrations remain almost unchanged. In the far IR region metal-fluoride and metal-ligand vibrations have been assigned to establish the stereochemistry of the complexes. On complexation new bands appear in the 300-340 cm^{-1} region which are attributable to ν(M-N) modes. In the $SnF_4(bfq)_2$, $SnF_4(boq)_2$, $TiF_4(bfq)_2$ and $TiF_4(boq)_2$ complexes the appearance of only one ν(M-F) band at 550, 540, 560 and 580 cm^{-1}, respectively, indicates a trans-octahedral geometry.

A five coordinated trigonal bipyramidal or a hexacoordinated octahedral structure involving fluorine bridged bonds can be assigned to the 1:1 complexes of zirconium (IV) fluoride. A polymeric trans-octahedral structure involving fluorine bonds (30) has earlier been postulated for the 1:1 amine adducts of group (IV) metal tetrafluorides. In the $ZrF_4(bfq)$ and $ZrF_4(boq)$ complexes two ν(Zr-F) bands appear at 460, 350 cm^{-1} and 480, 370 cm^{-1}, respectively which are attributable to the terminal and bridged ν(Zr-F) vibrations. The bridged ν(Zr-F) vibration seems to be shifted to lower spectral region (134, 153) by 110 cm^{-1} in each case. The position of the terminal ν(Zr-F) vibrations in these complexes is in the region as reported for the hexacoordinated complexes of zirconium (IV) fluoride (160). Thus, the $ZrF_4(bfq)$ and $ZrF_4(boq)$ complexes are postulated as octahedral complexes involving fluorine bridging.

TABLE - 11

Assignments of IR spectra (4000-200 cm^{-1}) of bfq, bcq and their complexes

Assignments	bfq	$SnF_4(bfq)_2$	$TiF_4(bfq)_2$	$ZrF_4(bfq)$	bcq	$SnF_4(bcq)_2$	$TiF_4(bcq)_2$	$ZrF_4(bcq)$
ν(C=C)and ν(C=N)	1600w 1580w 1560w 1485sh 1445vvs	1605w 1580w 1570m 1490w 1455vs	1635s 1625m 1585m 1505s 1452vs	1635s 1618s 1590m 1555s 1452vvs	1615s 1585m 1570s 1540w 1520m	1612m 1582m 1570m 1520sh	1632m 1612w 1598m 1575w 1518w	1635w 1610sh 1600s 1550w 1530w
CH in plane def.	998m 975w	995m 970w	995s 780w	1020s 970w	970s	970s	962m	970s
CH def.	710s	700s	720s	715sh	720vs	720vs	712vs	710s
ν(M-X)		550s	560vvs	460vs 350s		540m,b	580vs,b	480m 370m
ν(M-N)		325w	300s	325w		325w	305m	340w

REFERENCES

1. R.K. Ingham, S.D. Rosenberg and H. Gilman; Chem. Rev., 60, 459 (1960).
2. D. Quane and R.S. Bottei; Chem. Rev., 63, 403 (1963).
3. A.G. Davies; Chem. Britain, 4, 403 (1968).
4. F. Glockling; Quart. Rev., 20, 45 (1966).
5. O.H. Johnson; Chem. Rev., 48, 259 (1951).
6. R.F. Rolsten and H.H. Sisler; J. Am. Chem. Soc., 79, 1068 (1957).
7. H.H. Sisler, H.H. Batey, B. Pfahler and R. Mattair; J. Am. Chem. Soc., 70, 3021 (1948).
8. H.H. Sisler, E.E. Shilling and W.O. Groves; J. Am. Chem. Soc., 73, 426 (1951).
9. R.C. Aggarwal and P.P. Singh; J. Inorg. Nucl. Chem., 28, 1651 (1966).
10. R.C. Aggarwal and P.P. Singh; J. Inorg. Nucl. Chem., 28, 1655 (1966).
11. I.R. Beattie; Quart. Rev., 17, 382 (1963).
12. S.E. Livingstone; Quart. Rev., 19, 386 (1965).

13. M. Akbar Ali and S.E. Livingstone; Coord. Chem. Rev., 13, 101 (1974).

14. J.E. Fergusson, W.R. Ropper and C.J. Wilkins; J. Chem. Soc., 3716 (1965).

15. O.A. Osipov, U.L. Shelepina and O.B. Shelepin; Zh. Obshch. Khim., 36, 264 (1966).

16. W.R. Trost; Can. J. Chem., 30, 855 (1952).

17. H.C. Poller and D.L.B. Toley; J. Chem. Soc.(A), 1578 (1967).

18. M. Lesbre, P. Mazerolles and J. Satge; 'The Organic Compounds of Germanium', Interscience Publishers, London, 539 (1971).

19. R. Schwarz and F.W. Schenk; Chem. Ber., 63, 296 (1930).

20. J.S. Thomas and Th. Pugh; J. Chem. Soc., 60 (1931).

21. J.S. Thomas and W.W. Southwood; J. Chem. Soc., 2083 (1931).

22. W. Eisenbuth and J.R. Van Wazer; Inorg. Nucl. Chem. Lett., 3, 359 (1967).

23. C.H. Yoder and J.J. Zuckermann; Inorg. Chem., 3, 1329 (1964)

24. N. Serpone and R.C. Fay; Inorg. Chem., 8, 2379 (1969).

25. R.C. Fay and T.J. Pinnavaia; Inorg. Chem., 7, 508 (1968).

26. S.C. Jain and R. Rivest; Can. J. Chem., 41, 2130 (1963).

27. S.A.A. Zaidi and T.A. Khan; Ind. J. Chem., 15A, 461 (1977).

28. R. Rivest; Can. J. Chem., 40, 2234 (1962).

29. A.A. Woolf; J. Inorg. Nucl. Chem., 3, 285 (1956).

30. E.L. Muetterties; J. Am. Chem. Soc., 82, 1082 (1960).

31. C.J. Wilkins and H.M. Haendler; J. Chem. Soc., 3174 (1965).

32. G. Marcotrigiano, G.C. Pellacani and C. Pretti; J. Inorg. Nucl. Chem., 36, 3709 (1974).

33. C.C. Scenney and R.J. Magee; Inorg. Nucl. Chem. Lett., 10, 323 (1974).

34. G. Durgaprasad, D.N. Sathyanarayana and C.C. Patel; Can. J. Chem., 47, 631 (1969).

35. D.M.L. Garg; Ind. Chem. Soc., 42, 339 (1965).

36. Cadwell; Chem. Abst., 23, 5353 (1929).

37. J. Chatt, L.A. Duncanson and L.M. Venanzi; Suomen Kemi., B29, 75 (1956).

38. S. Åkerström; Acta. Chim. Scand., 10, 699 (1956).

39. A. Fredga; Rec. Trav. Chim., 69, 416 (1950).

40. K. Glen and R. Schwale; Angew. Chem., 62, 320 (1950).

41. M. Honda, M. Komura, Y. Kawasaki, T. Tanaka and R. Okawara; J. Inorg. Nucl. Chem., 30, 3231 (1968).

42. F. Bonati, S. Cenini and R. Ugo; J. Organomet. Chem., 9, 395 (1967).

43. G. Aravamudan, D.H. Brown and D. Venkappayya; J. Chem. Soc.(A), 2744 (1971).

44. A. Hulanicki and L. Shishkova; Chem. Anal. (warsaw)., 10, 837 (1965).

45. D. Cook; Can. J. Chem., 43, 3322 (1965).

46. D.N. Satyanarayana and C.C. Patel; Ind. J. Chem., 5, 360 (1967).

47. A. Ravi, J. Gopalakrishan and C.C. Patel; Ind. J. Chem., 5, 356 (1967).

48. R.A. Bailey and T.R. Peterson; Can. J. Chem., 47, 1681 (1969).

49. B.E. Zaitsev, V.K. Akimov, A.I. Busev and S.I. Gusev; Zh Obshch. Khim., 35, 2119 (1965).

50. A.F. Bekhli, N.P. Kozyreva, Sh. D. Moshkovskii, S.A. Robinovich, E.V. Maksakovkaya, V.F. Gladkinkh, M.M. Lebedeva M.D. Lychko and N.Ya. Soprunova; Med. Parazitol. Parazit. Bolezni. (Russ), 46, 71 (1977).

51. F.M. Sharabi, J.P. Long and J.G. Cannon; J. Pharmacol. Exp. Ther., 202, 97 (1977).

52. B. Janos, G. Marcel, S. Fernand and B. Karl; Helv. Chim. Acta, 60, 598 (1977).

53. B.N. Cookburn, D.V. Howe, T. Keating, B.F.G. Johnson and J. Lewis; J. Chem. Soc.(A), 404 (1972).

54. E.O. Fischer, H.A. Goodwin, C.G. Kreiter, H.D. Simmons Jr, K. Sonogashira and S.B. Wild; J. Organomet. Chem., 14, 359 (1968).

55. G.L. Vaughan; Chem. Abst., 79, 115732 p, (1973).

56. L.J. Bellamy; 'The Infrared Spectra of Complex Molecules', Methuen, London, 249, 257 (1958).

57. C.N.R. Rao; 'Chemical Applications of Infrared Spectroscopy', Academic Press, New York, 318, 327 (1963).

58. O. Piovesana and C. Furlani; J. Inorg. Nucl. Chem., 32, 879 (1970).

59. E. Spinner; J. Chem. Soc., 1237 (1960).

60. D.J. Brown and S.F. Mason; 'The Pyrimidines', Interscience Publishers, London, 494 (1962).

61. D.J. Brown, E. Hoerger and S.F. Mason; J. Chem. Soc., 4035 (1955).

62. S.F. Mason; J. Chem. Soc., 3619 (1958).

63. C.N.R. Rao; 'Chemical Applications of Infrared Spectroscopy', Academic Press, New York, 250 (1963).

64. L.J. Bellamy; 'The Infrared Spectra of Complex Molecules', Methuen, London, 278, 282 (1958).

65. R.C. Lord, A.L. Wartson and F.A. Miller; Spectrochim. Acta, 9, 113 (1957).

66. L.J. Bellamy; 'The Infrared Spectra of Complex Molecules', Methuen, London, 351, 355 (1958).

67. Randall, Fowler, Fuson and Dangl; 'Infrared Determination of Organic Structures', Van Nostrand (1949).

68. D.H. Sweeney, S. Mizushima and C.V. Cuagliano; J. Am. Chem. Soc., 77, 6521 (1955).

69. R.B. Hannan Jr, J.H. Leiblich and A.G. Renfrew; J. Am. Chem. Soc., 71, 3733 (1949).

70. L.J. Bellamy; 'The Infrared Spectra of Complex Molecules', Methuen, London, 268 (1958).

71. R.H. Wiley and S.C. Slaymaker; J. Am. Chem. Soc., 79,2233 (1957).

72. I.A. Brownlie; J. Chem. Soc., 3062 (1950).

73. L.N. Short and H.W. Thompson; J. Chem. Soc., 168 (1952).

74. K. Nakanishi; 'Infrared Absorption Spectroscopy', Nankodo Company Limited, Tokyo, 42, 48 (1962).

75. L.J. Bellamy; 'The Infrared Spectra of Complex Molecules', Methuen, London, 134, 209 (1958).

76. A. Albert and E. Spinner; J. Chem. Soc., 1221 (1960).

77. E. Spinner; J. Chem. Soc., 1226, 1232 (1960).

78. R.A. Katritzky and R.A. Jones; J. Chem. Soc., 2949 (1960).

79. D.J. Brown and L.N. Short; J. Chem. Soc., 331 (1953).

80. H.W. Thompson, D.L. Nicholson and L.N. Short; Disc. Farad. Soc., 9, 222 (1950).

81. S.F. Mason; J. Chem. Soc., 4874 (1957).

82. Tanner; Spectrochim. Acta, 8, 9 (1956).

83. J.I. Jones, W. Kynaston and J.L. Hales; J. Chem. Soc., 614 (1957).

84. E. Spinner; J. Org. Chem., 23, 2037 (1958).

85. A. Yamaguchi, R.B. Penland, S. Mizushima, T.J. Lane, C. Curran and J.V. Quagliano; J. Am. Chem. Soc., 80, 527 (1958).

86. M. Davies and W.J. Jones; J. Chem. Soc., 955 (1958).

87. E. Spinner; Spectrochim. Acta, 95 (1959).

88. C.N.R. Rao 'Chemical Applications of Infrared Spectroscopy', Academic Press, New York, 300 (1963).

89. D.T. Elmore; J. Chem. Soc., 3489 (1958).

90. R.K. Goswi, U. Aggarwal and C.N.R. Rao; J. Am. Chem. Soc., 89, 235 (1967).

91. I. Suzuki; Bull. Chem. Soc. Japan, 35, 1286, 1456 (1962).

92. C.N.R. Rao and R. Venkataraghavana; Spectrochim. Acta, 18, 541 (1962).

93. K. Nakamoto; 'Infrared Spectra of Inorganic and Coordination Compounds', John Wiley and Sons, Inc., New York, 103, 106 (1963).

94. K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', John Wiley and Sons, Inc., New York, 118 (1963).

95. T.L. Brown and M. Kubota; J. Am. Chem. Soc., 83, 4175 (1961).

96. I.R. Beattie and M. Webster; J. Chem. Soc., 3672 (1965).

97. I.R. Beattie, G.P. McQuillan, L. Rule and M. Webster; J. Chem. Soc., 1514 (1963).

98. I.R. Beattie, G. Gibson, M. Webster and G.P. McQuillan; J. Chem. Soc., 238 (1964).

99. I.R. Beattie, M. Milne, M. Webster, H.E. Blayden, P.J. Jones, R.C.G. Killean and J.L. Lawrence; J. Chem. Soc.(A), 482 (1969).

100. I.R. Beattie, T.R. Gilson and G.A. Ozin; J. Chem. Soc.(A), 2772 (1968).

101. I.R. Beattie, R. Hulme and L. Rule; J. Chem. Soc., 1581 (1965).

102. I. Douek, M.J. Fraser, Z. Geffer, M. Goldstein, B. Rimmer and H.A. Willis; Spectrochim. Acta, 23A, 375 (1967).

103. T. Tanaka, Y. Matsumura, R. Okawara, Y. Musya and S. Kinumaki; Bull. Chem. Soc. Japan, 41, 1497 (1968).

104. J.P. Clark, V.M. Langford and C.J. Wilkins; J. Chem. Soc.(A), 792 (1967).

105. I.R. Beattie, M. Webster and G.W. Chantry; J. Chem. Soc., 6172 (1964).

106. N.N. Greenwood, B.P. Straughan and A.E. Wilson; J. Chem. Soc.(A), 2209 (1968).

107. A.D. Allen, F. Bottomley, R.O. Harris, V.P. Reinsalu and C.V. Senoff; J. Am. Chem. Soc., 89, 5595 (1967).

108. D.P. Ames and P.G. Sears; J. Phys. Chem., 59, 16 (1965).

109. C.M. Harris and A.D. Mackenzie; J. Chem. Soc.(A), 746 (1969).

110. N. Katsaros and J.W. George; J. Inorg. Nucl. Chem., 31, 3503 (1969).

111. G.J. Sutton; Aust. J. Chem., 20, 1859 (1967).

112. W. Rosen and D.H. Busch; Inorg. Chem., 9, 262 (1970).

113. K.W. Bagnall, D. Brown, P.J. Jones and J.G.H. du Preez; J. Chem. Soc., 3594 (1965).

114. W.J. Geary; Coord. Chem. Rev., 7, 81 (1971).

115. S.K. Madan and A.M. Donohue; J. Inorg. Nucl. Chem., 28, 1303 (1968).

116. M.D. Joesteen; Inorg. Chem., 6, 1598 (1967).

117. R.A. Mackay and R.F. Schneider; Inorg. Chem., 6, 549 (1967).

118. F.P. Lanrest and M.D. Joeslen; Inorg. Chem., 7, 2048 (1968).

119. V.V. Savant, P. Ramamurthy and C.C. Patel; J. Less Common Metals., 22, 479 (1970).

120. C.P. Prabhakaran and C.C. Patel; Indian J. Chem., 10, 438 (1972).

121. M.S. Golitskaya and K.N. Mekhalevich; Visn. L'viv. Politekh. Inst., 60, 28 (1971).

122. V.T. Panyushkin, A.D. Garnovskii, I.I. Grandberg, O.A. Osipov, V.I. MinKin, V.S. Troitskaya and V.G. Vinokurov; Zh. Obshch. Khim., 38, 1154 (1968).

123. D.Kh. Petkova, S.Ya. Shnaiderman and E.N. Knyazeva; Zh. Obshch. Khim., 42, 2236 (1972).

124. M. Blasekova and H.L. Schlaefer; Z. Anorg. Chem., 360, 169 (1968).

125. G. Brauer, 'Handbook of Preparative Inorganic Chemistry', Academic Press, New York, 730, 733 and 735 (1963).

126. N.H. Furman; 'Standard Methods of Chemical Analysis', Van Nostrand Co., Inc., 374 (1950).

127. C.J. Rodden; 'Analytical Chemistry of the Manhattan Project', McGraw-Hill Book Co., Inc., 374 (1950).

128. G. Charlot and D. Bezier; 'Quantitative Inorganic Analysis', Methuen, London, 609 (1955).

129. A.R. Katritzky; Quart. Rev., 13, 353 (1959).

130. G. Zerbi and G. Alberti; Spectrochim. Acta, 19, 1270 (1963).

131. R.R. Randle and D.H. Whiffin; 'Molecular Spectroscopy Reports of the Confrence of Institute of Petroleum'., (Oct. 1954).

132. O. Piovesana and C. Furlani; J. Inorg. Nucl. Chem., 32, 879 (1970).

133. I.R. Beattie and L. Rule; J. Chem. Soc., 3267 (1964).

134. R.J.H. Clark and C.S. Williams; Inorg. Chem., 4, 350 (1965).

135. S.A.A. Zaidi, T.A. Khan and M.S. Siddiqi; Acta. Chim. Acad. Sci. Hung., 92, 387 (1977).

136. S.A.A. Zaidi and T.A. Khan; Ind. J. Chem., 15A, 313 (1977).

137. A. Hulanicki; Talanta., 14, 1371 (1967).

138. D. Coucouvanis; Progress in Inorganic Chemistry, Edited by F.A. Cotton, Interscience Publishers John Wiley and Sons., Inc. New York, Vol 11, 234 (1970).

139. R. Eisenberg; Progress in Inorganic Chemistry, Edited by F.A. Cotton, Interscience Publishers John Wiley and Sons., Inc. New York, Vol 12, 295 (1970).

140. D.C. Bradley and M.H. Gitlitz; J. Chem. Soc.(A), 1152 (1969).

141. F. Ponati and R. Ugo; J. Organometal. Chem., 10, 257 (1967).

142. C. Preti and G. Tosi; J. Inorg. Nucl. Chem., 38, 1746 (1976).

143. J. Tombeux, L.C. Van Poucke and Z. Eckhaut; Spectrochim. Acta, 28A, 1943 (1972).

144. K. Nakamoto; 'Infrared Spectra of Inorganic and Coordination Compounds', John Wiley and Sons, Inc. New York, 155 (1963).

145. M. Colapietro, A. Domenicano and A. Vaciago; Chem. Comm., 572 (1968).

146. C.O. Connor, I.D. Gilbert and G. Wilkinson; J. Chem. Soc.(A), 1398 (1969).

147. R.W. Jones and R.C. Fay; Inorg. Chem., 12, 2599 (1973).

148. L. Juergen, H. Norbert and B. Klaus; Chem. Ber., 106(7), 2185 (1973).

149. Y.A. Simonov, S.P. Suntova, V.F. Ivanov, L.N. Milkova, Y.V. Yablokov, T.I. Malinauskii and A.V. Ablov., Chem. Abst. 80, 113583n (1974).

150. G. Diana, P. Ion, C. Aglaia, B. Marcel, N. Voiculescu and R. Lucia; Rev. Roum. Chem., 15, 1581 (1970).

151. N.N. Greenwood and K. Wade; Chem. Soc., 1130 (1960).

152. N.S. Gill, R.H. Nuttall, D.E. Scaife and D.W.A. Sharp; J. Inorg. Nucl.Chem., 18, 79 (1961).

153. G.E. Coates and D. Ridley; J. Chem. Soc., 166 (1964)

154. S.C. Jain; J. Inorg. Nucl. Chem., 35, 505 (1973).

155. S.A.A. Zaidi, K.S. Siddiqi and (Mrs.) N.S. Neelam; Ind. J. Chem., 14, 209 (1976).

156. S.A.A. Zaidi and K.S. Siddiqi; Z. Anorg. Algem. Chem., 379, 329 (1970).

157. S.A.A. Zaidi and K.S. Siddiqi; J. Inorg. Nucl. Chem., 35, 655 (1973).

158. A.D. Adley, D.F.R. Gilson and M. Onyszchuk; Chem. Comm., 813 (1968).

159. R.C. Aggarwal, T. Parsad and B.N. Yadav; J. Inorg. Nucl. 37, 899 (1975).

160. R.J.H. Clark and W. Errington; J. Chem. Soc.(A), 258 (1967).